Title

Controlling Groundwater Contamination from Oil and Gas Well Stimulation Practices and Leaking Underground Storage Tanks

Author

Toumari, Arman

Publication Date

2020

UNIVERSITY OF CALIFORNIA

Los Angeles

Controlling Groundwater Contamination from Oil and Gas Well Stimulation Practices and Leaking Underground Storage Tanks

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Environmental Science and Engineering

by

Arman Toumari

2020

ABSTRACT OF DISSERTATION

Controlling Groundwater Contamination of Fluoride from Matrix Acidization and Tertiary Butyl Alcohol from Leaking Underground Storage Tanks

by

Arman Toumari

Doctor of Environmental Science and Engineering in Environmental Science and Engineering

University of California, Los Angeles, 2020

Professor Irwin H. Suffet, Chair

This thesis addresses two major groundwater pollution problems: high fluoride concentrations in groundwater from matrix acidization, and release of tertiary butyl alcohol (TBA) from Leaking Underground Storage Tanks (LUSTs) into the groundwater. High fluoride concentrations are detrimental. Aluminum (Al^{3+}) and iron (III) (Fe^{3+}) ions in the subsurface can prevent the fluoride removal. This paper shows that calcium carbonate can precipitate 200 milligrams per liter (mg/L) of fluoride and 200 mg/L of aluminum or iron (III) in batch mode. Fluoride removals of up to 95% were achieved when dissolved calcium carbonate was used at a $[Ca^{2+}]/[F^-]$ molar ratio of 2:1. Aluminum or iron (III) ions did not hinder, and in some instances, improved the fluoride removal. PHREEQC geochemical model was consistent with the findings.

Since the 1980's, LUSTs have released millions of gallons of petroleum products containing TBA into the groundwater. TBA was banned in early 2000. The United States Environmental Protection Agency (EPA) considers TBA to be potentially carcinogenic to humans based on its proven carcinogenicity to animals. The State of California has a non-enforceable notification level (NL) of 12 micrograms per liter (μg/L) but has not established a maximum contaminant level (MCL) in drinking water for TBA. Toxicity, sources, and environmental transformation related to TBA are discussed; developing an

MCL, addition of TBA as a contaminant of concern in the California Water Resources Control Board's "Low Threat Closure Policy", and developing more stringent protocols for TBA treatment are recommended.

As high as 88% of LUST sites in Southern California were closed with TBA higher than its NL between 2016 and 2019 fiscal years (FY). 25% of the time, TBA concentrations remained higher than 2,300 µg/L during 2016-2017 FY, higher than 7,600 µg/L during 2017-2018 FY, and higher than 4,434.3 µg/L during 2018-2019 FY. The maximum TBA plume lengths increased as much as 70% from 2016 to 2019. Aerobic bioremediation, currently the most effective method of treating TBA, was employed at only one site. Reducing TBA to safe levels requires specific and a targeted treatment approach.

The dissertation of Arman Toumari is approved.

Jennifer Ayla Jay

Timothy Malloy

Michael K. Stenstrom

Irwin H. Suffet, Committee Chair

University of California, Los Angeles

2020

I dedicate this to my wife, Dr. Elham Hazany, whose support, encouragement, and sacrifice inspired me to go forward and make my dream a reality.

Table of Contents

Page

List of Figures

List of Tables

List of Equations

List of Symbols

Al^{3+}: aluminum ion
AlF_3: aluminum fluoride
$Al(OH)_3$: aluminum hydroxide
Ba^{2+}: barium ion
$CaCO_3$: Calcium carbonate (calcite)
Cd^{2+}: cadmium ion
CaF_2: calcium fluoride (fluorite)
$-CH_3$: methyl group
F^-: fluoride ion
Fe^{3+}: iron(III) ion
$FeCl_3$: iron(III) chloride
FeF_3: iron(III) fluoride
H_2O_2: hydrogen peroxide
NaOH: sodium hydroxide
O_3: ozone
API: American Petroleum Institute
AS: air sparging
bgs: below ground surface
BTEX: benzene, toluene, ethylbenzene, xylenes
CAA: Clean Air Act
CO_2: carbon dioxide
DIPE: di-isopropyl ether
DOGGR: Division of Oil, Gas, and Geothermal Resources
DPE: dual phase extraction
SCAQMD: South Coast Air Quality Management District
EPA: Environmental Protection Agency
ETBE: ethyl tertiary butyl ether
erf: error function
exp: exponential function
FY: fiscal year
GAMA: Groundwater Ambient Monitoring and Assessment
H&S: health and Safety
HCl: hydrochloric acid
HF: hydrofluoric acid
H_2: hydrogen
K_{oc}: carbon to water partitioning coefficient
K_{ow}: octanol/water partitioning coefficient
LARWQCB: Los Angeles Regional Water Quality Control Board
LNAPL: light non-aqueous phase liquid
LTCP: low-threat closure policy
LUFT: leaking underground fuel tank
LUST: leaking underground storage tank
Max: maximum
MCL: maximum contaminant level

μg/m^3: micrograms per cubic meters
μg/L: micrograms per liter
mg/m^3: milligrams per cubic meters
mg/kg: milligrams per kilogram
mg/L: milligrams per liter
MTBE: methyl tertiary butyl ether
NI: not implemented
NIH: National Institute of Health
NL: notification level
PAH: poly-aromatic hydrocarbon
PHREEQC: pH Redox Equilibrium (in C language)
PM1: methylibium petroleiphilum
RWQCB: Regional Water Quality Control Board
SB4: California Senate Bill 4
SI: saturation index
SVE: soil vapor extraction
SVOC: semi-volatile organic compound
SWRCB: State Water Resources Control Board
TAME: tertiary amyl methyl ether
TBA: tertiary butyl alcohol
TISAB: total ion selective addition buffer
TPH: total petroleum hydrocarbons
TPHd: total petroleum hydrocarbons as diesel
TPHg: total petroleum hydrocarbons as gasoline
UST: underground storage tank
VAFB: Vandenberg Air Force Base
VOC: volatile organic compound

I would like to thank

My advisor, Dr. Irwin H. (Mel) Suffet whose brilliant advice, kind support, smart encouragements, tireless edits and corrections, and belief in me, paved the way for me to come to this point. From the first moment of speaking to him on the phone when all this began, I knew that I couldn't ask for a better advisor. I would not have been here without him.

My doctoral committee members, Dr. Jennifer Jay, Dr. Tim Malloy, and Dr. Michael Stenstrom for their invaluable advice and comments on my work.

Mr. Harrison Levy of the Institute of Environment and Sustainability who had all the answers I needed regarding logistics.

The following persons from the Los Angeles Water Quality Control Board:

Dr. Yue Rong and Dr. Yi Lu for supporting me and graciously allowing me to focus my time on this project.
Dr. Weixing Tong for his recommendations and technical assistance on this project.
Mr. Joseph Luera, Ms. Amanda Davatolhagh, Mr. Ricky Huang, and Ms. Daisy Aurora Ojeda for their valuable assistance in collecting and analyzing data.

Arman Toumari

Education

Master of Environmental Engineering, City College of New York, February 2000
Master of Chemical Engineering, City College of New York, September 1994

Publications

Toumari, A., Stenstrom, M., and Suffet, I. H. (Mel) "Impact of Aluminum and Iron (III) Ions on Removal of Fluoride Ion (F^-) by Calcite". Environmental Engineering Science, Volume 36, Number 11, 2019, DOI: 10.1089/ees.2019.0189

Experience

Lecturer, Santa Monica College, Santa Monica, California, June 2004 – Present
Lecture General Chemistry and Supervise laboratory experiments.

Lecturer, Moorpark College, Moorpark, California, September 2003 – June 2004
Lecture General Chemistry and Supervise laboratory experiments.

Lecturer, Golden West College, Huntington Beach, California, February 2000 – June 2003
Lecture General Chemistry and Supervise laboratory experiments.

Lecturer, Los Angeles City College, Los Angeles, California, February 2000 – June 2003
Lecture General Chemistry and Supervise laboratory experiments.

Lecturer, Kingsborough Community College, Brooklyn, New York, September 1993 – October 1999
Lecture General Chemistry and Supervise laboratory experiments.

Water Resources Control Engineer, Water Quality Control Board, October 1999 - Present
Review corrective and remedial action plans for hydro-geologic investigations and field inspections.

Environmental Engineer, Department of Environmental Conservation, New York, October 1999 - Present
Assessment of wastewater treatment systems for compliance with State and Federal environmental regulations.

Professional Licenses

- California Professional Chemical Engineering License
- New York Professional Environmental Engineering License

Chapter 1: Introduction

Oil and gas well stimulation practices and leaky underground storage tanks (LUSTs) are important sources of pollution that can threaten the groundwater and drinking water resources in Southern California. This thesis addresses a major groundwater pollution problem from each of these sources

- high fluoride release from matrix acidization
- tertiary butyl alcohol (TBA), the toxin and known carcinogen in animal studies released from gasoline LUSTs.

Well stimulation practices, such as matrix acidization, can produce fluids containing high fluoride concentrations. High fluoride concentrations are detrimental, and since these fluids are frequently injected into the subsurface, they can contaminate our groundwater or drinking water resources.

LUSTs can also contribute to groundwater contamination. To increase fuel's octane rating, oxygenates such as methyl tertiary butyl ether (MTBE) and tertiary butyl alcohol (TBA) were added to gasoline for almost twenty years until their use was banned in early 2000. Since the 1980's, LUSTs in Southern California have released millions of gallons of petroleum products containing MTBE and TBA into the subsurface, which contaminated the soil and groundwater. TBA is also formed from biodegradation of MTBE as a second source in groundwater. TBA is extremely soluble in water and difficult to treat. TBA can be harmful to the human health and the environment. United States Environmental Protection Agency (EPA) considers TBA to be potentially carcinogenic to humans based on its proven carcinogenicity to animals.

This thesis is divided into four parts:

Part I covers a practical method of removing fluoride from the fluids produced by matrix acidization using calcium carbonate (calcite). The efficiency of this method in the presence of aluminum and iron (III) ions was determined. The experimental results were confirmed by a geochemical modeling software.

Part II is a critical literature review and evaluation conducted on TBA which includes a detailed discussion of chemical and physical properties, sources, health impacts, and current available treatment technologies of TBA. The critical literature review concluded that the toxicological evaluation of TBA indicated significant human health concerns. Thus, based upon the toxicological evidence, an MCL should be considered for TBA in drinking water. Also, the "Low Threat Closure Policy" adopted by the State Water Resources Control Board (SWRCB), which is a tool to evaluate LUST sites in California for closure, should cover TBA and require regulators to consider TBA contamination in soil or groundwater in their closure review. In addition, the fate of TBA in soil and groundwater indicated the biotransformation to form TBA and stability of TBA. Thus, California closure of LUST sites should be revisited, and a regulatory requirement should be considered for TBA contamination in soil and/or groundwater in closure reviews.

Part III is an analysis of TBA contamination in the groundwater on closed LUSTs sites in Southern California for the past three years. The analysis revealed that closing practices at Los Angeles Regional Water Quality Control Board (LARWQCB) should be more stringent towards TBA contamination. The steady increase of more than 70% of the maximum TBA plume lengths from 2016 to 2019 raises questions on whether it could reflect the LARWQCB's shift towards a more loosening policy on TBA contamination. This points to an increase risk of impact on the drinking water resources when considering the proximity of drinking water wells to the LUST sites in California.

In Part IV, remediation methods employed in LUST sites in LARWQCB jurisdiction were reviewed. Aerobic bioremediation appeared to be the most effective method of treating TBA contamination but was employed at only one case during the time investigated. The remedial methods were not nearly as effective in reducing the TBA concentrations as compared with MTBE which indicated that reducing TBA to safe levels in the groundwater requires a more specific and targeted approach.

Chapter 2

Impact of Aluminum and Iron (III) Ions on Removal of Fluoride by Calcite

Table of Contents Page

ABSTRACT

Matrix acidization adds high concentrations of hydrofluoric acid that is added into the production well and thus, the return fluids contain high fluoride ion concentrations. Depending on the fate of the return fluids, such high fluoride levels could negatively affect public health and/or the environment if it remains untreated.

Acidization techniques for well stimulation are in use throughout central California, especially in Kern Country, and throughout the Southern California region. There have been over 600 instances of acidizing in urbanized Southern and Central California from April 2013 to September 2015.

This paper shows that calcium carbonate can remove fluoride ions from simulated return waters containing 200 ppm of fluoride and 200 ppm of aluminum or iron (III) by precipitation mechanism in batch mode.

Fluoride ion concentrations were measured at fixed intervals during a three-hour period. The results showed fluoride removal efficiencies of up to 95% can be achieved when dissolved calcium carbonate is used at a

$[Ca^{2+}]/[F^{-}]$ molar ratio of 2:1 to remove 200 ppm fluoride from the simulated return water. Additionally, the presence of aluminum or iron (III) ions and their complexes did not hinder, and in some instances actually, improved the fluoride removal efficiency. The PHREEQC geochemical model was utilized as a predictive tool, which verified the study findings regarding the complexes and their role in chemical precipitation of fluoride compounds. Further studies are needed to evaluate other complexing agents, such as silicon complexes.

Keywords: matrix acidization return fluid, calcite, fluorite, fluoride removal, PHREEQC Geochemical Model

Introduction and Background

California has some of the highest reserves of oil in the world, and thus, oil and gas production remains a major California industry. For example, the Long Beach oil field in the Los Angeles Basin, once contained about 5 billion m^3 (3 billion barrels) of oil within an area of less than 7 km^2 (2,000 acres) (Long, et al., 2015). According to the California Division of Oil, Gas, and Geothermal Resources (DOGGR, 2017), there are 52 oil fields in the state, each with more than 16 million m^3 (100 million barrels) of known recoverable oil.

Over the last sixty years, well stimulation techniques, such as matrix acidizing, have been used to enhance oil and gas production as California oil fields mature. The modern-day era of acid use in well stimulation began in the 1930's when corrosion inhibitors were discovered to stop acid attack on metal. Commercial use of acids began in the 1950's (Williams et al., 1979). The idea of using acids for well stimulation or cleaning a wellbore is an old concept, but the chemicals, volumes, and techniques used in acidizing have changed.

Matrix acidizing is used to remove formation damage around the wellbore and/or increase reservoir permeability. Operators inject acid solutions, such as hydrofluoric acid (HF), hydrochloric acid (HCl), or mud acid (HF/HCl) into the well at pressures below fracture pressure (Robertson et al., 1989). Acids etch the reservoir silica rock creating channels for oil and gas to flow. The mechanisms involved include etching the mineral surfaces by dissolving the minerals and mobilizing particles by decomposing the rock structure (Mcleod, 1986). In California, matrix acidizing is conducted at depths ranging from 2,000-11,000 feet (Abdullah et al., 2016) and are in use throughout central California, especially in Kern Country, and throughout the Southern California region. From April 2013 to September 2015, over 600 instances of acidizing took place in urbanized Southern and Central California. During this period, the average amount of HF added during matrix acidizing events reported to California South Coast Air Quality Management District (SCAQMD) is 258 kg/treatment (Abdullah et al., 2016). The average amount of HF added during matrix acidizing events reported to DOGGR during the same period is 1,869 kg/treatment (Abdullah et al., 2016). Reacted HF leaves fluoride behind, and excessive fluoride can be detrimental (Abdullah et al., 2016). From September 2014 to September 2015, 23 matrix acidization activities were reported to DOGGR to comply with California Senate Bill 4 (SB4) enacted in 2013. SB4 sets the framework for regulation of well stimulation technologies in California. In all cases, the return fluids were discharged into underground injection control wells, which could potentially contaminate our groundwater and affect human health.

Shuchart (1995) analyzed several sets of well returns after HF acidizing treatments and reported Al^{3+} concentrations in a typical return fluid sample to range from 35 mg/L to 1,111 mg/L. Fe^{3+} concentrations in a typical return fluid sample ranged from 0 mg/L to 10,000 mg/L. The concentration (in mg/L) ratio of F^- to Al^{3+} ranged from 0.58 to 2.44.

Fluoride concentrations of greater than 1.5 mg/L in drinking water can cause fluorosis, and adverse effects have been found from fluoride concentrations as low as 0.5 mg/L (Ayoob and Gupta, 2007). High concentrations of fluoride, above levels causing dental fluorosis, have been detected in the groundwater in portions of aquifers in five desert regions of southern California, mainly the Coachella Valley (22%), the Colorado River basin (20%), the Mojave River area (10%), Owens Valley (3%), and the Antelope Valley (3%) (Wong, 2017). Discharging Matrix acidizing return fluids into the subsurface can add more fluoride to the already impacted groundwater and affect human health.

Several fluoride removal methods are currently in use, including coagulation and adsorption. Coagulation processes use chemical reagents such as lime, calcium, magnesium salts, poly aluminum chloride and alum to form a precipitant with fluoride (Wong, 2017). Adsorption uses sorption media that is often packed in columns. Water containing fluoride is cycled through the columns, and the media can be regenerated, renewed or disposed. The use of calcite to remove fluoride at concentrations of 5-10 mg/L from drinking water and wastewater has been extensively studied. Dissolution of calcite increases calcium concentration until saturation is reached and CaF_2 precipitation occurs. Precipitation of CaF_2 occurs only at higher concentrations of fluoride (10-20 mg/L or more) (Wong, 2017).

A few studies have also been conducted on fluoride removal by calcite in the presence of some specific metals. Cai et al. (2017) used calcite to remove fluoride in the presence of barium ions (Ba^{2+}) and cadmium ions (Cd^{2+}) at approximately 10 mg/L by a batch reactor and a column test. Cai et al. (2017) refers to the need to treat the fluoride impacted groundwater in Australia caused by leaching of the aluminum production byproduct, Spent Pot Lining (SPL). Ba^{2+} and Cd^{2+} are part of the chemical make-up of SPL. Results indicated that neither Ba^{2+} nor Cd^{2+} had any significant impact on fluoride removal. However, other metallic ions, such as Al^{3+} or Fe^{3+} have not been studied. In addition, no study focusing on fluoride removal from matrix acidizing return fluids which would address the complications associated with mineral–fluoride complexation has been published.

Objectives

This research is an early effort to develop a process to remove fluoride in presence of complex-forming Al^{3+} and Fe^{3+}. This is in anticipation of a potentially large environmental problem. Release of fluoride into surface waters can create large problems at drinking water treatment plants. Conventional water treatment technology does not remove fluoride, and treatment plants with high fluoride in their raw water (> 1.0 mg/L), have few options. Precipitation using calcite (an inexpensive substance) seems to be a promising methodology. The Los Angeles Regional Water Quality Control Board (LARWQCB) maintains an “Oil and Gas Operation” program to monitor and address issues relating to oil and gas operations and their impacts on surface and groundwater resources. Therefore, the results of this research can benefit the LARWQCB in evaluating the impacts of matrix acidization on groundwater resources and considering new regulations.

Methods and Data

Chemistry

Removal processes involving the ions of interest are governed by the reactions presented in Table 2-1. The formation of fluorite (CaF_2), aluminum fluoride (AlF_3), aluminum hydroxide ($Al(OH)_3$), and iron (III) hydroxide ($Fe(OH)_3$) depend on the solution pH as shown in Table 2-2.

Table 2-1. Removal Processes Involving Calcium, Aluminum, and Iron

Reaction (Precipitation)	Ksp[a]
$Ca^{2+}(aq) + CO_3^{2-}(aq) \leftrightharpoons CaCO_3(s)$	3.3×10^{-9}
$Ca^{2+}(aq) + 2F^-(aq) \leftrightharpoons CaF_2(s)$	8.5×10^{-11}
$Al^{3+}(aq) + 3OH^-(aq) \leftrightharpoons Al(OH)_3(s)$	3×10^{-34}
$Al^{3+}(aq) + 3F^-(aq) \leftrightharpoons AlF_3(s)$	2×10^{-17}
$Fe^{3+} + 3OH^- \leftrightharpoons Fe(OH)_3(s)$	7.76×10^{-38}
Reaction (Complex Formation)	K[b]
$Al^{3+} + F^- \rightleftarrows AlF^{2+}$	$10^{6.12}$
$Al^{3+} + 2F^- \rightleftarrows AlF_2^+$	$10^{11.15}$
$Al^{3+} + 3F^- \rightleftarrows AlF_3$	10^{15}
$Al^{3+} + 4F^- \rightleftarrows AlF_4^-$	$10^{17.74}$
$Al^{3+} + 5F^- \rightleftarrows AlF_5^{2-}$	$10^{19.37}$
$Al^{3+} + 6F^- \rightleftarrows AlF_6^{3-}$	$10^{19.84}$

Reaction (Complex Formation)	K[c]
$Fe^{3+} + F^- \rightleftarrows FeF^{2+}$	$10^{5.2}$
$Fe^{3+} + 2F^- \rightleftarrows FeF_2^+$	$10^{10.6}$
$Fe^{3+} + 3F^- \rightleftarrows FeF_3$	$10^{13.7}$
$Fe^{3+} + 4F^- \rightleftarrows FeF_4^-$	N/A
$Fe^{3+} + 5F^- \rightleftarrows FeF_5^{2-}$	N/A
$Fe^{3+} + 6F^- \rightleftarrows FeF_6^{3-}$	N/A

[a] Generalic, Eni. "Solubility Product Constants", www.periodni.com/solubility_product_constants.html

[b] Complexation Equilibrium Coefficients (J.D. Hem, Chemistry of Aluminum in Natural Water, 1968)

[c] Complexation Equilibrium Coefficients (J. Inczedy, Analytical Applications of Complex Equilibria, 1976)

Table 2-2. The pH Dependence of Calcium, Aluminum, Iron and Silica Chemistry in Return Fluid Waters

Reaction
$Ca^{2+}(aq) + 2F^-(aq) + H^+ + CO_3^{2-} \leftrightharpoons CaF_2(s) + HCO_3^-$
$Al^{3+}(aq) + 3OH^-(aq) \leftrightharpoons Al(OH)_3(s)$
$Al_2Si_2O_5(OH)_4(s) + 18HF(aq) \rightarrow 2H_2SiF_6(aq) + 2AlF_3(s) + 9H_2O(l)$
$Fe^{3+}(aq) + 3OH^-(aq) \leftrightharpoons Fe(OH)_3(s)$

Experimental Design

This study was conducted in two phases as shown in Table 2-3. In phase I, calcite was used in solid state. In phase II, calcite was used in aqueous state. "Blank sample" refers to the mixture of NaF + $CaCO_3$. "Al-sample" refers to the mixture of NaF + $AlCl_3$ + $CaCO_3$. "Fe-sample" refers to the mixture of NaF + $FeCl_3$ + $CaCO_3$. "Combined (Al^{3+} + Fe^{3+}) sample" refers to the mixture of NaF + $AlCl_3$ + $FeCl_3$ + $CaCO_3$.

Table 2-3. Amounts and Concentrations of Reagents Used in the Study

Sample	Na^+ (mg/L)	F^- (mg/L)	Al^{3+} (mg/L)	Fe^{3+} (mg/L)	Cl^- (mg/L)	NaF (mg)	$AlCl_3$ (mg)	$FeCl_3$ (mg)	CaCO3	
									Phase I (g)	Phase II (mg/L)
Blank	241	200	---	---	---	176	---	---	13.32	900
Al-Sample	241	200	200	---	790	176	396	---	13.32	900
Fe-Sample	241	200	---	200	380	176	---	232	13.32	900
Al+Fe Sample	241	200	200	200	1179	176	396	232	13.32	900

Volume of Deionized Water = 400 mL

Phase I

For this study, sodium fluoride, aluminum chloride, and iron (III) chloride were dissolved in 400 mL of distilled water to produce solutions with starting concentrations of 200 mg/L each for F^-, Fe^{3+}, and Al^{3+} ions. 13.32 grams of solid calcite was then added to the solutions. The solutions were continuously stirred and were either analyzed immediately or left for two days to reach equilibrium, as done by Cai et al., (2017). Fluoride concentration and pH were measured over a 3-hour period.

Phase II

For this study, sodium fluoride, aluminum chloride, and iron (III) chloride were dissolved in 400 mL of distilled water to produce solutions with starting concentrations of 200 mg/L each for F^-, Fe^{3+}, and Al^{3+} ions. Calcite was completely dissolved in distilled water by lowering the pH using HCl to achieve a concentration of 900 mg/L for calcite in each case as described in Table 2-3. This concentration of calcite was used to achieve a $[Ca^{2+}]/[F^-]$ molar ratio of approximately 2:1 and to ensure a fluoride limiting environment.

The pH was raised to the desired value using NaOH as shown on the pH plots indicating the starting pH. Solutions were continuously stirred and were analyzed for fluoride and pH over a 3-hour period.

Experimental Protocol

Fluoride concentration was measured using an Ion Selective Electrode (American Scientific Corporation, Portland, Oregon, USA) and a Silver Chloride 900100, Single Junction, Reference Electrode (Thermo Fisher Scientific, Waltham, Massachusetts, USA) following the procedure below:

1. Using solid NaF, a 1000 mg/L fluoride stock solution was prepared in "Total Ion Selective Addition Buffer" (TISAB) III (Aqua Solutions, Inc., Deer Park, Texas, USA). The stock solution was then diluted to make standards of the following concentrations prepared with the addition of TISAB III.
    a. 500 mg/L
    b. 100 mg/L
    c. 50 mg/L
    d. 10 mg/L
2. The sample to be analyzed was transferred into a clean dry beaker large enough to contain two electrodes. 10 mL of TISAB III was added for every 100-mL sample to be analyzed.
3. The potential difference of the standard solutions was measured by a PHI 350 Digital pH/temperature/mV meter (Beckman Coulter, Inc., Pasadena, California, USA). The lowest to highest concentration was followed considering the initial fluoride concentrations of the sample to be analyzed.
4. A clean and dry fluoride Ion Selective Electrode as well as reference electrode was inserted into the solution and was swirled gently.
5. The potential difference on the meter was recorded using the voltage scale after it was stabilized.

6. To determine the fluoride concentration of the sample to be analyzed, a standard calibration curve was prepared showing the measured potential difference versus the log of fluoride concentration.
7. A best-fit curve was created, and the equation of the curve was used to calculate the concentration of fluoride in the sample.

Plastic lab-ware was used for storage of standard solutions to prevent potential reaction of fluoride with glass over time.

Geochemical Modeling

PHREEQC software (Parkhurst and Appelo, 2013), a geochemical model for simulating chemical reactions and transport processes in natural or polluted water was used in this study. PHREEQC is capable of simulating chemical reactions, such as aqueous equilibria, mineral dissolution and precipitation, ion exchange, surface complexion, solid solutions, gas-water equilibrium, and kinetic biogeochemical reactions. The general framework for the PHREEQC simulations is presented in Figure 2-1.

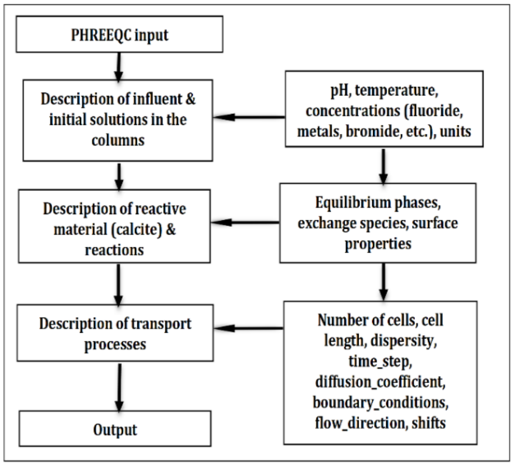


Figure 2-1. General Framework of PHREEQC Input File (Cai, et al. 2017)

The software was used as a speciation program to calculate saturation indices (SIs) and the distribution of aqueous metal/ fluoride species, and ultimately, to verify the experimental results as follows:

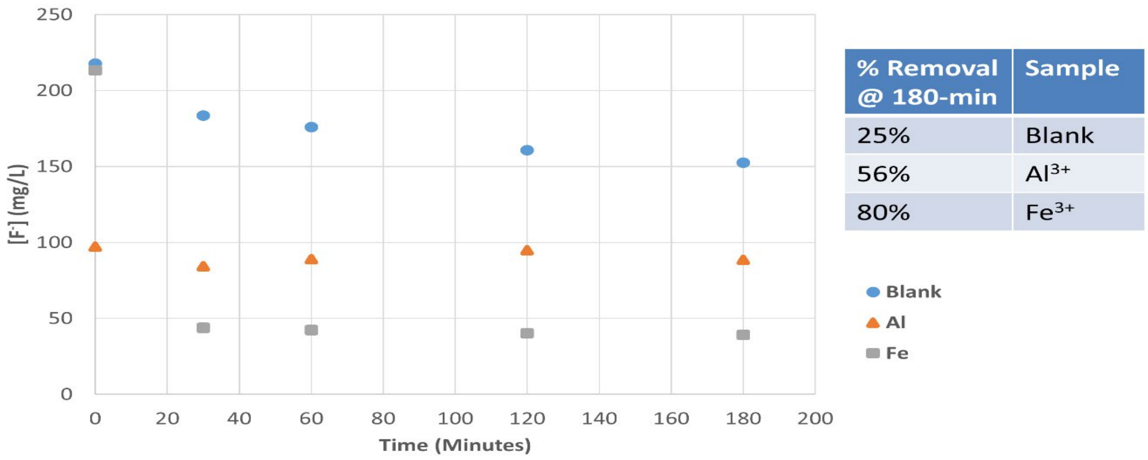
1. Solution composition, pressure and temperature were entered into the program.
2. The program was set to adjust the equilibrium pH in order to achieve charge balance.
3. The batch reaction modeling feature of the program was used to predict how the solution reacts with a solid phase or aqueous phase of $CaCO_3$.

Results

Phase I

- Immediate Analysis after Calcite Addition

Figure 2-2 shows that Fe^{3+} had a positive impact on fluoride removal by calcite. For example, at 180-minute mark, an 80% fluoride removal was achieved in the sample containing 200 mg/L Fe^{3+} as compared to a 25% fluoride removal in the blank sample. Al^{3+} also improved fluoride removal, but to a lesser extent. Although the starting concentration of fluoride in all cases was 200 mg/L, the concentration of fluoride dropped immediately upon measurement at time zero as shown on Figures 2-2, 2-4, 2-6, and 2-7. In some instances, the measured initial concentration of fluoride was slightly above the starting value of 200 mg/L which could be due to instrumentation error.



% Removal @ 180-min	Sample
25%	Blank
56%	Al^{3+}
80%	Fe^{3+}

Figure 2-2. Effect of 200 mg/L Al^{3+} and Fe^{3+} on Removal of 200 mg/L F$^-$
Samples were analyzed immediately after calcite addition

The pH of the solutions after the initial rise, was generally stable after 60 minutes.

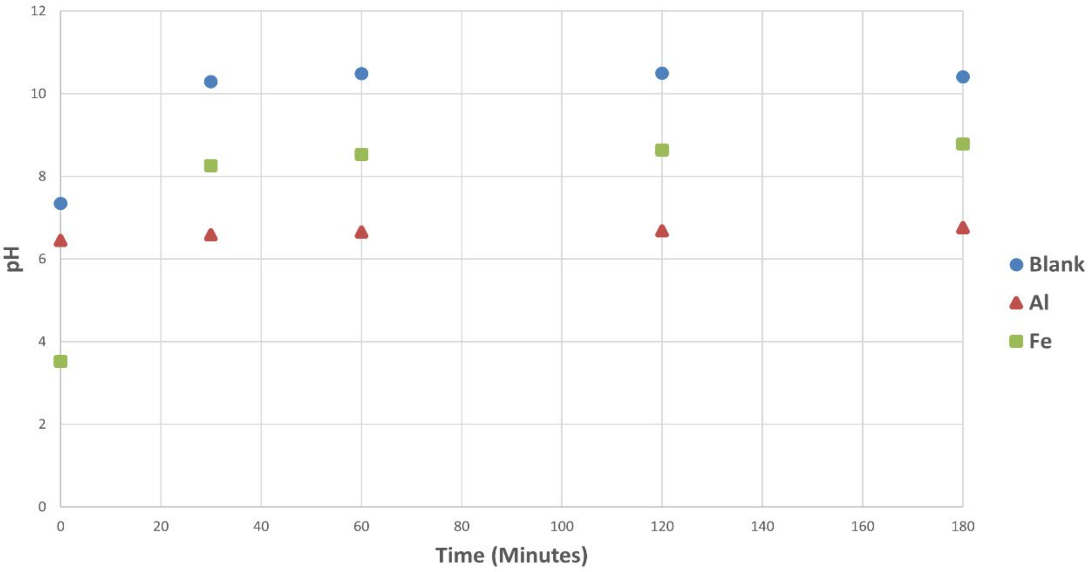


Figure 2-3. Effect of 200 mg/L Al^{3+} and Fe^{3+} on pH. Samples Analyzed Immediately After Calcite Addition.

The positive saturation indices of CaF_2 for all three cases calculated by PHREEQC (see Tables 2-4, 2-6, and 2-8) verify that fluoride removal is governed by the formation of CaF_2. Zero saturation indices calculated by PHREEQC for calcite for all three cases indicate that the calcium ions favor combining with the fluoride ions over the carbonate ions.

Table 2-4. Indices – Blank Sample

Phase	**SI**	**log IAP**	**log K_{sp} (298K, 1 atm)**
Calcite ($CaCO_3$)	0.00	-8.48	-8.48
Fluorite (CaF_2)	1.98	-8.09	-10.07

Table 2-5. PHREEQC Output - Blank Sample

Species	Concentration (mol/kg)
F^-	1.048×10^{-2}
NaF	5.079×10^{-5}
HF	1.688×10^{-9}
HF_2^-	6.791×10^{-11}

Equilibrium pH	9.92

In case of Al^{3+}, PHREEQC shows that considerable amounts of aqueous Al-F complexes including AlF_3 are expected (Table 2-7). However, a negative saturation index for AlF_3 suggests that AlF_3 is under-saturated, and the removal of fluoride is due only to the formation of solid CaF_2 (see Table 2-6).

Table 2-6. Indices – Al^{3+} Sample

Phase	**SI**	**log IAP**	**log K_{sp} (298K, 1 atm)**
$Al(OH)_3$	2.49	-31.51	-34
Calcite ($CaCO_3$)	0.00	-8.48	-8.48
Fluorite (CaF_2)	1.49	-9.11	-10.60
AlF_3	-2.04	-19.30	-17.27

Table 2-7. PHREEQC Output - Al^{3+} Sample

Species	Concentration (mol/kg)
AlF_2^+	2.986×10^{-3}
AlF_3	1.392×10^{-3}
AlF^{2+}	2.237×10^{-4}
F^-	5.327×10^{-5}
AlF_4^-	2.951×10^{-5}
NaF	2.233×10^{-7}
HF	1.553×10^{-8}
HF_2^-	3.175×10^{-12}

Equilibrium pH	6.627

In case of Fe^{3+}, as Table 2-8 shows, the positive saturation indices of CaF_2 and FeF_3 point to the likelihood that fluoride removal is achieved through the formation of both CaF_2 and FeF_3.

Table 2-8. Indices – Fe^{3+} Sample

Phase	**SI**	**log IAP**	**log K_{sp} (298K, 1 atm)**
$Fe(OH)_3$	4.75	-32.36	-37.11
Calcite ($CaCO_3$)	0.00	-8.48	-8.48
Fluorite (CaF_2)	3.79	-6.81	-10.60
FeF_3	2.49	-16.77	-19.26

Table 2-9. PHREEQC Output - Fe^{3+} Sample

Species	Concentration (mol/kg)
$Fe(OH)_2^+$	1.699×10^{-3}
$Fe(OH)_3$	1.196×10^{-3}
FeF_2^+	6.349×10^{-5}
$Fe(OH)_4^-$	8.219×10^{-6}
$FeOH^{+2}$	1.283×10^{-6}
FeF^{+2}	3.538×10^{-7}
$Fe_3(OH)_4^{+5}$	2.151×10^{-10}
$Fe_2(OH)_2^{+4}$	1.661×10^{-10}

Equilibrium pH	6.808

➢ Analysis Two Days after Calcite Addition

Figure 2-4 shows that the presence of Al^{3+} and Fe^{3+} significantly improved fluoride removal for samples left for two days before analysis. For example, at 180-minute mark, 85% fluoride removal was achieved in the sample containing 200 ppm Fe^{3+} as compared to 27% fluoride removal in the blank sample.

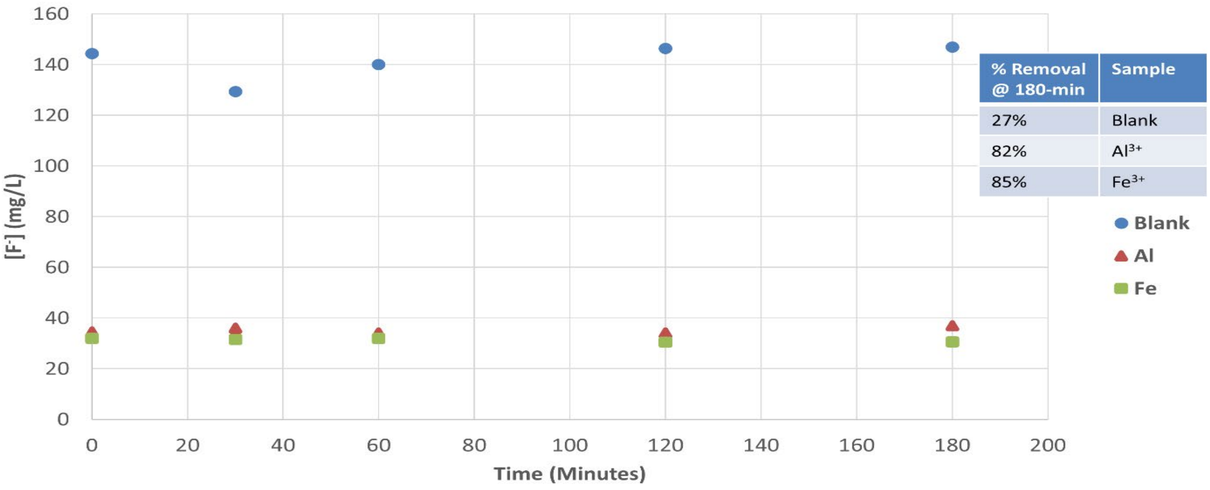


Figure 2-4. Effect of 200 mg/L Al^{3+} and Fe^{3+} on Removal of 200 mg/L F^-. Samples Left for 2 Days before Analysis.

Fluoride removal was slightly improved compared to the samples containing Fe^{3+} analyzed immediately after calcite addition (85% vs. 80%, see Figure 2-2). Figure 2-5 shows that the pH of the solutions in each case was generally constant throughout the reaction.

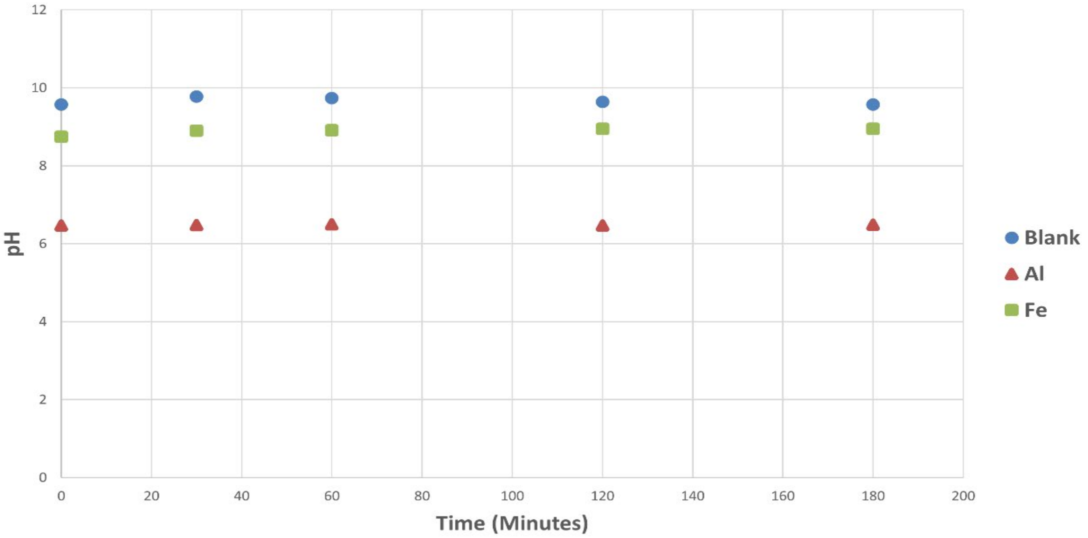
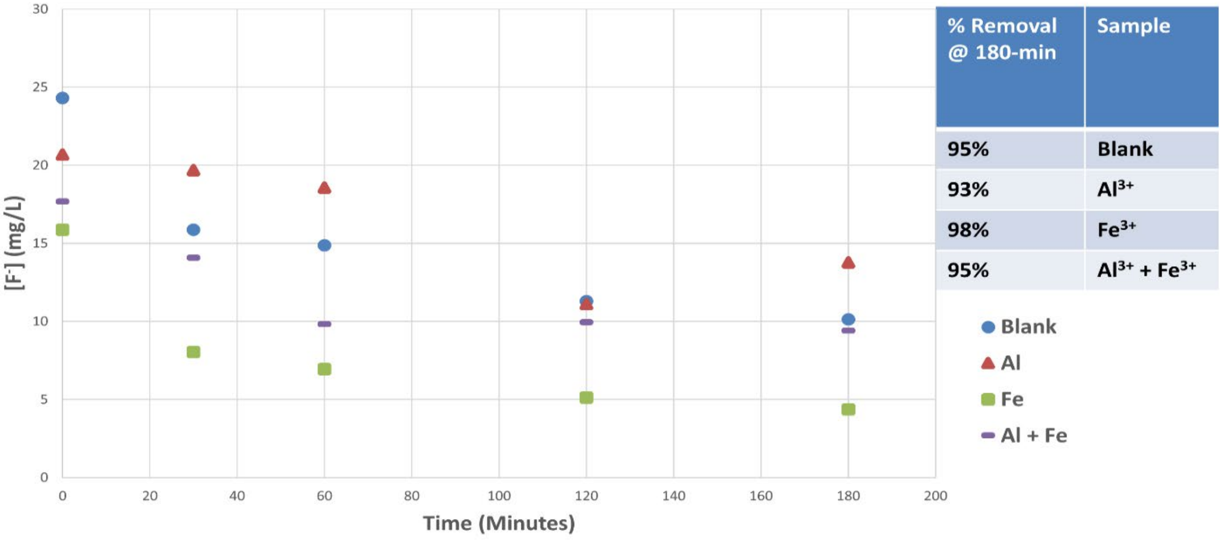


Figure 2-5. Effect of 200 mg/L Al^{3+} and Fe^{3+} on pH. Samples Left for 2 Days before Analysis.

Phase II

In Phase II, a combined (Al^{3+}+ Fe^{3+}) sample was investigated. As Figures 2-6 and 2-7 show, the fluoride removal efficiency in the combined (Al^{3+}+ Fe^{3+}) samples was second best after Fe^{3+} samples.



% Removal @ 180-min	Sample
95%	Blank
93%	Al^{3+}
98%	Fe^{3+}
95%	Al^{3+} + Fe^{3+}

Figure 2-6. Effect of 200 mg/L Al^{3+} and Fe^{3+} on Removal of 200 mg/L F^- at Starting pH =10. Calcite Made Completely Soluble.

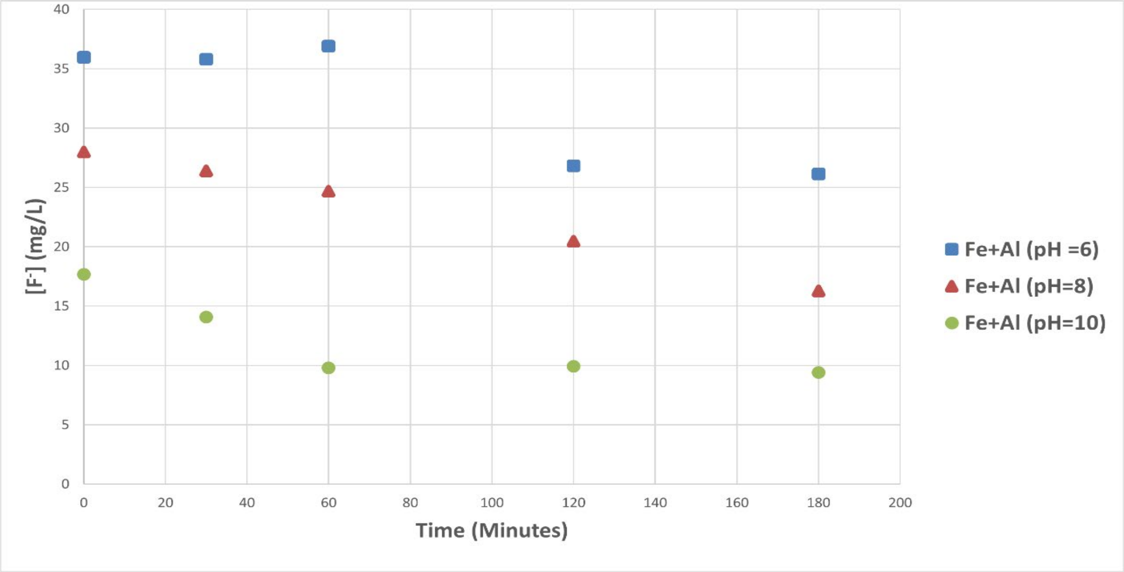


Figure 2-7. Effect of 200 mg/L (Al^{3+} + Fe^{3+}) Combined on Removal of 200 mg/L F^- at Different Starting pH.

The presence of Fe^{3+} and Al^{3+} ions enhanced fluoride removal when calcite was made completely soluble. As Figure 2-7 shows, the combined (Al^{3+}+ Fe^{3+}) samples performed best at pH of 10. Since the recovered fluids will likely contain iron and aluminum ions, the pH should be raised to 10 to obtain the highest removal. In addition, allowing solid calcium carbonate to dissolve completely in the return fluid offers much better fluoride removal compared with using solid calcium carbonate. The positive saturation index of CaF_2 (Table 2-10) indicates that fluoride removal is achieved through the formation of CaF_2.

Tables 2-10 and 2-11 present PHREEQC outputs for the combined (Al^{3+} + Fe^{3+}) samples.

Table 2-10. Indices – Combined Fe^{3+} & Al^{3+} sample

Phase	**SI**	**log IAP**	**log K_{sp} (298K, 1 atm)**
$Fe(OH)_3$	5.11	-32.00	-37.11
Calcite ($CaCO_3$)	2.00	-6.48	-8.48
Fluorite (CaF_2)	3.59	-7.01	-10.60
Hematite (Fe_2O_3)	24.01	20.01	-4.01
Geothite (FeOOH)	11.00	10.00	-1.00
$Al(OH)_3$	1.18	-32.82	-34

Table 2-11. PHREEQC Output – Combined Fe^{3+} & Al^{3+} sample

Species	Concentration
$Al(OH)_4^-$	6.077×10^{-3}
$Fe(OH)_3$	2.75×10^{-3}
AlF_4^-	9.173×10^{-4}
AlF_3	4.106×10^{-4}
$Fe(OH)_2^+$	1.003×10^{-4}
$Fe(OH)_4^-$	7.367×10^{-4}
$Al(OH)_3$	1.091×10^{-5}

Discussion

This research was focused on answering the question of whether Al-F and Fe-F complexes might interfere with calcite's ability to precipitate fluoride at high concentrations. This research was a laboratory scale project which simulated the actual conditions on the field during matrix acidization operation. The PHREEQC geochemical model verified the lab study findings regarding the complexes and their role in chemical precipitation of fluoride compounds in the presence of both Al^{3+} and Fe^{3+} ions. As the results show, the fluoride removal process in the presence of both Al^{3+} and Fe^{3+} ions was most efficient at pH of 10. Therefore, a starting pH of 10 in the soluble calcite scenario is recommended. The presence of silicon may complicate our findings, and therefore, needs to be further researched. In addition, the cost effectiveness of the method presented should be further studied. Due to the limited amount of information available to the public on the specifics of matrix acidizing operation, very few sources for referencing analytical data on actual return fluid samples were available. California Senate Bill 4 requires matrix acidizing operators to report analytical results of return fluid sampling. However, there are limitations associated with self-reported information. Therefore, a system that would allow government agencies to access the wells being stimulated or acidized is needed, so that split samples of actual return fluids can be collected and analyzed independently. Also, obtaining an actual return fluid sample from the matrix acidization operation could lead to a more accurate assessment of the treatment methodology and efficiency. Further studies will be needed to investigate the presence of other minerals, such as silicon.

Conclusions

- The fluoride removal process in the presence of both Al^{3+} and Fe^{3+} ions was most efficient at pH of 10. Therefore, a starting pH of 10 in the soluble calcite scenario is recommended.
- The presence of silicon may complicate our findings, and therefore, needs to be researched.
- The cost effectiveness of the method presented should be further studied.
- A system that would allow government agencies to access the stimulated or acidized wells is needed, so that split samples of actual return fluids can be collected and analyzed independently.
- Obtaining an actual return fluid sample from the matrix acidization operation could lead to a more accurate assessment of the treatment methodology and efficiency.

References

Abdullah, K, Malloy, T, Stenstrom, M. J., and Suffet, I. H. (Mel) (2016). Toxicity of Acidization Fluids Used in California Oil Exploration. *Toxicological & Environmental Chemistry Journal*. 99, 1.

Ayoob, S. and Gupta, A.K. (2007). Fluoride in Drinking Water: A Review on the Status and Stress Effects, *Critical Reviews in Environmental Science and Technology*. 36, 433.

Cai, Q, Turner, B. D., Sheng, D., and Sloan S. (2017). Impact of Barium and Cadmium on Defluoridation by Calcite: Batch Reactor and Column Tests. *Journal of Environmental Engineering Science*. 34, 792.

Division of Oil, Gas, and Geothermal Resources (DOGGR) (2017). *Annual Report of California Oil and Gas Production Statistics*. California Department of Conservation Documents. Available at: www.conservation.ca.gov/dog/pubs_stats/annual_reports/Pages/annual_reports.aspx

Generalic, E. (2019). *Solubility Product Constants. EniG. Periodic Table of the Elements. KTF-Split*. Available at: www.periodni.com/solubility_product_constants.html.

Hem, J. D. (1968). Aluminum Species in Water. U.S. Geological Survey, Menlo Park, California: American Chemical Society Publications, p. 98.

Inczedy, J. (1977). Analytical Applications of Complex Equilibria. *Journal of Chemical Education.* 54, 467.

Long, J., Birkholzer, J. T., and Feinstein, L. C. (2015). *Advanced Well Stimulation Technologies in California*. California Council on Science and Technology, Lawrence Berkeley National Laboratory, Pacific Institute. Available at: https://ccst.us/publications/2015/160708-sb4-vol-II.pdf

McLeod, H.O. (1986). *Matrix Acidizing to Improve Well Performance, Short Course Manual.* Society of Petroleum Engineers. Richardson, Texas. Available at https://www.petrowiki.org/matrix_acidizing

Parkhurst, D.L., and Appelo, C.A.J. (2013). Description of Input and Examples for PHREEQC Version 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations: *U.S. Geological Survey Techniques and Methods*. p. 497. Available at: https://pubs.usgs.gov/tm/06/a43/

Robertson, J. Jr, Chilingarian, G., and Kumar, S. (1989). Surface Operations in Petroleum Production. *Acidizing Oil Wells*. New York: Elsevier Science Publishing Company, p. 171.
Williams BB, Gidley JL, Schechter RS (1979). Acidizing fundamentals*.* Monograph Series. Richardson, Texas: Society of Petroleum Engineers, Chapters 2, 5, 9

Shuchart, C. E. (1995). HF Acidizing Returns Analyses Provide Understanding of HF Reactions. Presented at the *Society of Petroleum Engineers European Formation Damage Symposium*, The Hague, Netherlands, May 15-16.

Wong, E.Y., Stenstrom, M.K. (2017). Onsite Defluoridation System for Drinking Water Treatment using Calcium Carbonate. *Journal of Environmental Management* 216, 270.

Chapter 3

Evaluation of Tertiary Butyl Alcohol (TBA) Impact on Groundwater: Application to California

Table of Contents Page

ABSTRACT

Leaking Underground Storage Tanks (LUSTs) contribute to groundwater contamination. Since the 1980's, LUSTs in Southern California have released millions of gallons of petroleum products containing fuel oxygenates, methyl tertiary butyl ether (MTBE) and tertiary butyl alcohol (TBA) into the subsurface, which contaminated the soil and groundwater. These oxygenates were banned in early 2000 because they can harm the human health. The United States Environmental Protection Agency (EPA) considers TBA to be potentially carcinogenic to humans based on its proven carcinogenicity to animals. The State of California has not established a maximum contaminant level (MCL) for TBA.

This critical literature review provides information on the toxicity and sources of TBA and environmental transformation related to TBA from MTBE. Thus:

1. Despite numerous documented environmental and health hazards, TBA has not received sufficient attention from government agencies. The toxicological evaluation of TBA indicates significant human health concerns. Based upon the available toxicological evidence, an MCL should be developed for TBA.
2. The California Water Resources Control Board's "Low Threat Closure Policy", which is a tool to evaluate closure of LUST sites, does not mention TBA nor does it require regulators to consider TBA contamination in soil or groundwater in their closure review. This should be revisited based upon the toxicity data, the biotransformation of TBA from MTBE, and the stability of TBA in the environment.
3. TBA lacks a maximum contaminant level (MCL) in California. TBA is considered a non-regulated chemical by the California Health Department. Therefore, the current health-based level for TBA in drinking water established by the California Health Department, called "notification level" (NL)

or “action level" of 12 micrograms per liter (μg/L), is solely “advisory” and not enforceable. Despite numerous documented health hazards, TBA has not received sufficient attention from government agencies. The toxicological evaluation of TBA indicates significant human health concerns. Thus, an MCL should be considered for TBA in drinking water.

4. This review aims to raise awareness regarding the magnitude of the TBA problem in groundwater and urges government regulators to develop more stringent protocols for TBA treatment before closing LUST sites. The nine Regional Water Quality Control Boards (RWQCB) regulate and oversee cleanup at LUST sites in the State of California. Therefore, the results of the TBA study in California will directly impact RWQCB regulatory practices related to TBA and will help provide a framework for developing monitoring and cleanup strategy for TBA around the world.

Keywords: Tertiary Butyl Alcohol, Methyl Tertiary Butyl Ether, Underground Storage Tanks, Groundwater Contamination, Fuel Oxygenates

Introduction

Tertiary butyl alcohol (TBA) is one of the fuel oxygenates used to replace tetra-ethyl lead as an anti-knock agent in gasoline alone or with methanol as a co-solvent. Adding small amounts of oxygenates to gasoline can replace significant amounts of octane (Clark, 2001). Oxygenates replaced tetra-ethyl lead after it was banned in the 1980's by the EPA. Following the 1990 Federal Clean Air Act (CAA) Amendments, several oxygenate, including ethers (e.g., methyl tertiary butyl ether (MTBE), di-isopropyl ether (DIPE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME)) and alcohols (e.g., ethanol or TBA) were considered (Shih et al., 2004). MTBE was the main oxygenate due to its lower cost and favorable transfer and blending characteristics. However, TBA was also used as fuel oxygenate and octane booster in unleaded gasoline.

TBA is often detected in groundwater after oxygenated fuel spills. TBA in groundwater can originate from three different sources. First, as a direct addition to fuels as octane booster (American Petroleum Institute (API), 2012). Second, as a small impurities added along with MTBE or ETBE (Shell Global Solutions, 2003; ITRC, 2005). Third, as a biotransformation product of MTBE degradation (Schmidt et al., 2004; DeVaull et al., 2003; API, 2012). At several leaking underground storage tanks (LUST) sites, the concentration of TBA in groundwater is far greater than what can be expected from TBA as the primary oxygenate in the spilled gasoline (Wilson and Adair, 2007). Based on the ratio of TBA to MTBE at gasoline LUST sites in Orange County, California, Wilson et al., (2005) showed how TBA occurring from biodegradation of MTBE could explain the concentrations of TBA at 85% of the sites evaluated. A confounding issue in this analysis of TBA in groundwater samples was the possible formation of TBA as a result of hydrolysis of MTBE to TBA during sample preservation and analytical methods used (O'Reilly et al., 2001; Lin, Wilson, and Fine, 2003). However, Rong and Kerfoot, (2003) showed that the data from their three case studies did not support acid preservation of groundwater samples contributing to MTBE hydrolysis to form TBA (Rong and Kerfoot, 2003).

Substantial amounts of fuel oxygenates can enter the subsurface from a failing underground storage tank (UST). Therefore, TBA contamination in groundwater and potentially in drinking water supplies can be primarily caused by LUST sites releasing MTBE and TBA. TBA is still detected in the groundwater even though the use of MTBE in gasoline was banned in many states in the early 2000s (Fiorenza et al., 2002). According to Shih et al. (2004), fuel oxygenates are more harmful to groundwater resources compared to other petroleum constituents (e.g., benzene, toluene, ethylbenzene, and xylenes [BTEX]). Compared to BTEX, fuel oxygenates have significantly higher polarity, and thus more water soluble. They are also less adsorbed to soil particles, and therefore move farther and faster in groundwater (Shih et al., 2004). TBA also resists biodegradation. Therefore, it remains in soil and groundwater (National Institutes of Health (NIH), 2007). Kane et al., (2001) reports that TBA may accumulate and persist in some sediments even with relatively low concentrations of MTBE, and BTEX compounds may even exacerbate this process.

The objective of this critical literature review is to discuss the TBA's groundwater sources, fate and transport, potential human health hazards, and determine whether it is necessary to have more robust regulation and enforcement of TBA. California will be used as the area of concern, as California has been the largest user of fuel oxygenates (Shih et al., 2004). This makes California an important environmental indicator for the national impacts of TBA. Shih et al., (2004) have shown the locations of many LUST sites in California as an example of the magnitude of the MTBE and TBA problem. Shih et al., (2004) also examined fuel hydrocarbons and oxygenates at 868 LUST sites from the Los Angeles, CA region and reported that "excluding the composite measure total petroleum hydrocarbons as gasoline (TPHg), TBA had the greatest site maximum (geometric mean) groundwater concentration among the analytes studied" (Shih et al., 2004). A resolution adopted in 2004 by the California State Water Resources Control Board (SWRCB) revised regulations in California Code of Regulation and mandated the responsible parties of LUST sites to submit laboratory analytical data to the SWRCB's Geotracker Database (http://geotracker.waterboards.ca.gov). This paper reviewed the Geotracker data on the remediation status of approximately 8,770 sites with TBA contamination throughout California.

Production and Use

TBA is a man-made substance and produced in large quantities (NIH, 2007). It is manufactured by the catalytic hydration of isobutylene or by the reduction of tert-butyl hydroperoxide (Clark, 2001). TBA can also be formed from tertiary butyl acetate (TBAc) which degrades both biologically and chemically to TBA. In addition, TBA is a co-product of commercial propylene oxide production. Microorganisms that grow on volatile n-alkanes and bacteria that grow on isobutane can generate TBA. The primary source of isobutane is natural gas seeps (API, 2012).

TBA has several applications, such as paint removing, nail polishing, production of plastics, flavors, and perfumes (NIH, 2007). TBA can also be used to coat metals, in industrial cleaning products, and in pharmaceutical applications (USEPA, Office of Environmental Health Hazard Assessment, 1999). The wide range of industrial and household applications of TBA raises concern about its potential human health effects.

Toxicity of TBA and Public Health Considerations

Depending on the magnitude of exposure, TBA can irritate eyes, skin, and mucous membrane, or cause narcosis. Skin contact can cause slight redness or contact dermatitis (The Hazardous Substances Data Bank (HSDB), 1985). Other sources (Patty's Industrial Hygiene and Toxicology, 1982) have indicated similar effects, such as eye, nose, and throat irritation, headache, nausea, fatigue, and dizziness.

Animal studies (EPA Toxicological Review, 2017) have reported kidney, thyroid, and neurodevelopmental effects resulting from chronic oral exposure to TBA and reduced fetal viability and increased skeletal variations in acute oral or inhalation exposure. The same study (EPA Toxicological Review, 2017) associated renal tumors in male rats and thyroid tumors in female mice to potential carcinogenicity in humans. SWRCB has also confirmed these findings (SWRCB, 2020).

Some studies (Amberg et al., 2000; Hong et al., 1999; EPA, 2017) have identified TBA as one of the primary metabolites of MTBE and ETBE. Following an average of 90.1 mg/m^3 and 757 mg/m^3 doses of MTBE, TBA was measured to have a half-life of 8.1 ± 2.0 hours in the human urine. Following an average of 104 mg/m^3 and 210 mg/m^3 doses of ETBE, TBA was measured to have a half-life of 7.9 ± 2.7 hours in the human urine (Nihlén et al., 1998). The results of these studies raise concern regarding consuming water contaminated with MTBE or ETBE.

TBA lacks a maximum contaminant level (MCL) in California. TBA is considered a non-regulated chemical by the California Health Department. Therefore, the current health-based level for TBA in drinking water established by the California Health Department, called “notification level” (NL) or “action level", is solely “advisory” and not enforceable. Currently, an NL of 12 micrograms per liter (μg/L) has been assigned for TBA. The Division of Drinking Water (DDW) of the SWRCB confirms that “NLs are advisory in nature and not enforceable standards.” If a chemical is present in drinking water that is provided to consumers at concentrations considerably greater than the NL, DDW recommends that the drinking water system take the source out of service. The level prompting a recommendation for source removal is the "response level" of Health and Safety Code §116455, and depends upon the toxicological endpoint that is the basis for the notification level. The response level for TBA has been set at 100 times its NL, or 1,200 μg/L (SWRCB 2020).

Despite numerous documented health hazards, TBA has not received sufficient attention from government agencies. The toxicological evaluation of TBA indicates significant human health concerns. Thus, an MCL should be considered for TBA in drinking water.

Data Analyses

There are nine Regional Water Quality Control Boards (RWQCB) statewide established based on watersheds in California (Figure 3-1). Table 3-1 and Figures 3-2 and 3-3 show a review of Geotracker data on the concentrations of TBA (in µg/L) detected in the groundwater beneath LUST sites throughout California in 2019 categorized by the California Water Quality Control Board regions (Geotracker Database [http://geotracker.waterboards.ca.gov]).

LUST sites are particularly important because they represent major point sources of gasoline constituents and are the leading cause of oxygenate groundwater contamination. An extensive search of Geotracker revealed that in LUST sites overseen by the Los Angeles Regional Water Quality Control Board (LARWQCB) alone, which comprises of Los Angeles, Ventura counties, and portions of Kern and Santa Barbara counties, some 5,000 known releases of gasoline have occurred by the end of 2019. Approximately 50% of the LUST sites in LARWQCB are located within 1-mile radius of a drinking water production well based upon the data search of Geotracker. The TBA data shows that the maximum TBA concentrations exceeded the NL of 12 µg/L in 95% of the sites.

Older EPA methods (8020 or 8021) were used for groundwater analyses before 1999. These methods did not report concentrations of TBA. The newer methods 8260 or 8260B which utilize “purge and trap” method directing the samples through gas chromatography and a mass spectrometer detector replaced the old methods in 2000 and 2001 (Wilson et al., 2005). The groundwater concentrations of TBA in this study were reported by laboratories certified by SWRCB Environmental Laboratory Accreditation Program using EPA Method 8260B.

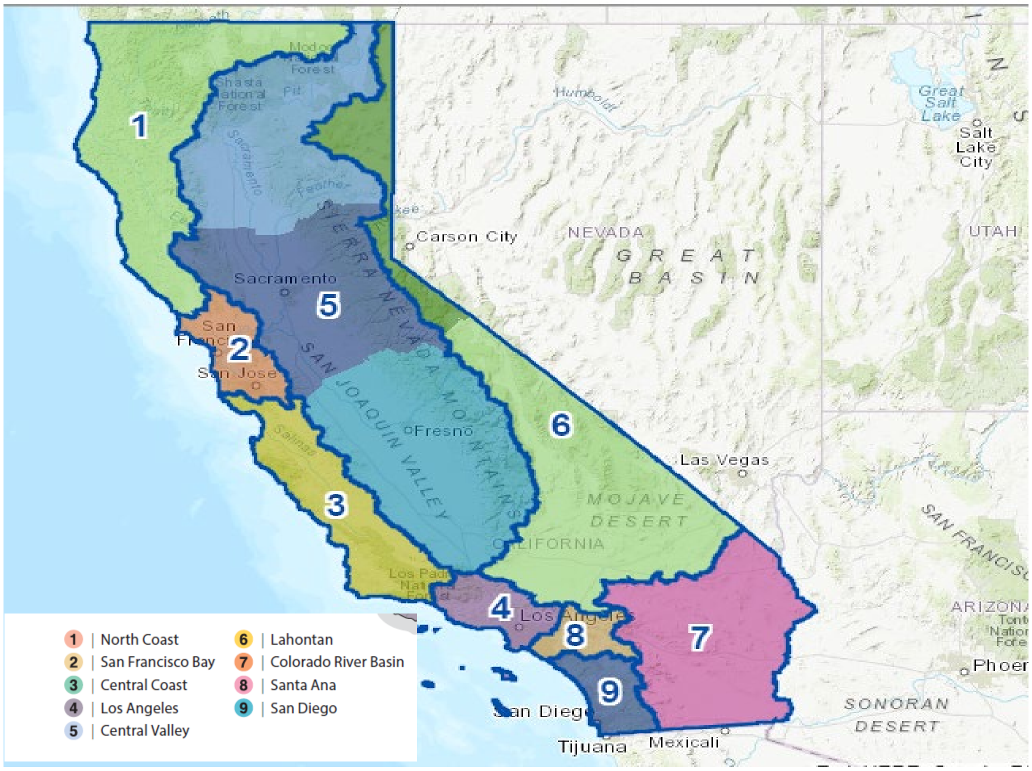


Figure 3-1. California Water Quality Control Board Regions (CWQCR)

Table 3-1. Summary Statistics on LUST Site of TBA Concentrations in Groundwater throughout the CWQCBR 2019

Highest Site TBA Concentration Detected (µg/L)	Regional Water Quality Control Board Regions (R)								
	R-1	R-2	R-3	R-4	R-5	R-6	R-7	R-8	R-9
Minimum	3.84	5.4	4.6	3.5	1.44	4.08	33	7.2	15
Maximum	7000	562,00	58,100	2,200,00	260,00	273,000	14,80	88,20	20,00
Median	155	540	100	1,200	248	272.5	1,100	1,800	12,50
25th Percentile	65.75	84.25	16	137.5	50.425	8.75	200	100	399
75th Percentile	400	3,750	900	15,000	1,700	5,243.1	3,000	11,60	16,00

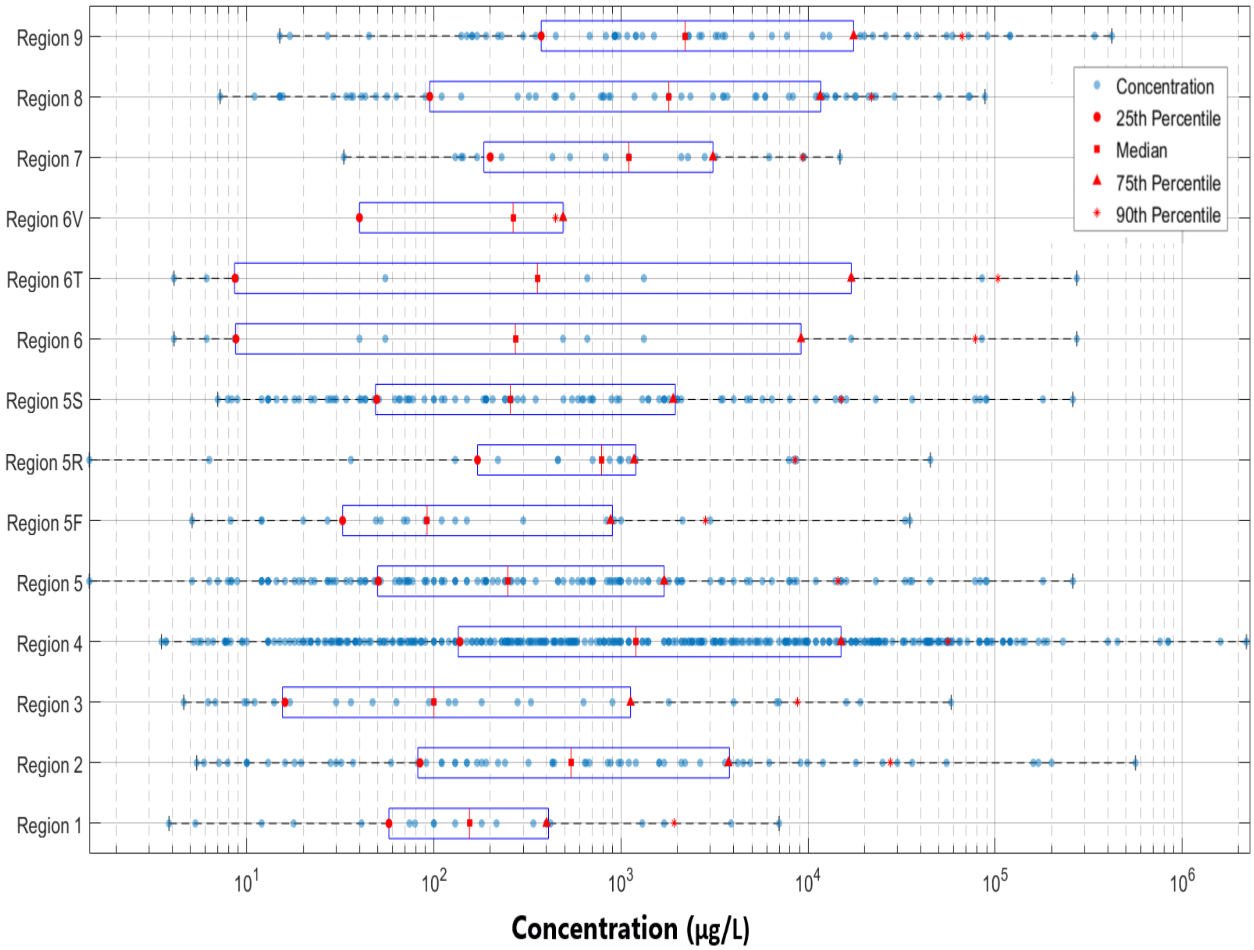
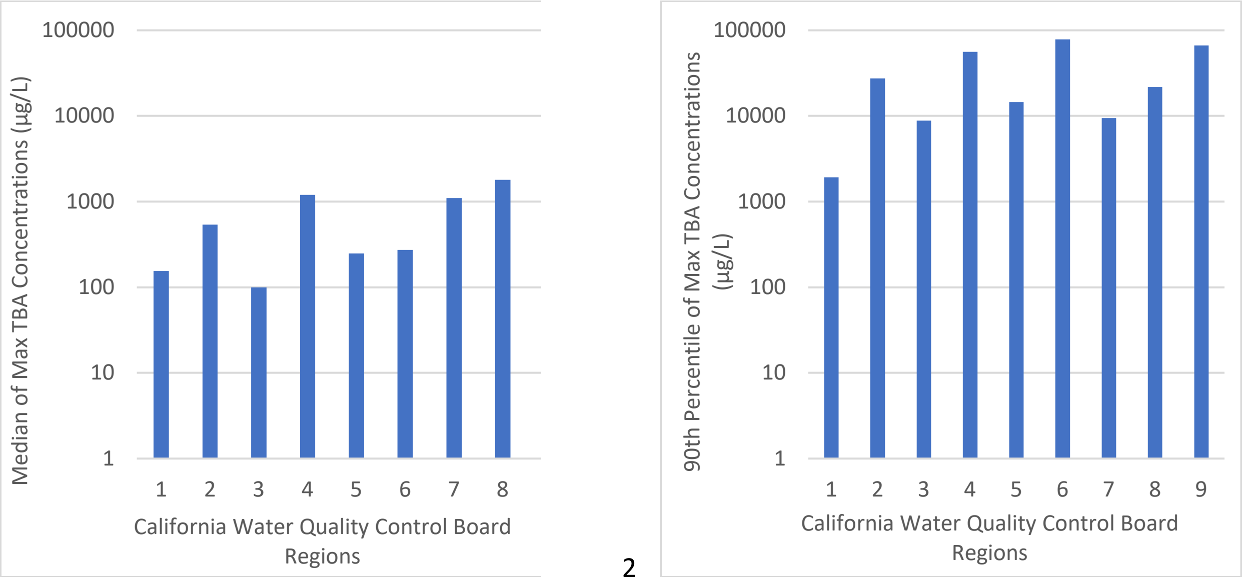


Figure 3-2. Summary statistics on LUST site TBA concentrations in the Nine Regional Boards shown on Figure 3-1 in 2019

Figure 3-3 shows that the median TBA concentrations among all Regions were highest in Regions 4, 7, 8, and 9 with median TBA concentrations in Regions 4, 7, and 8 falling into a relatively narrow range of 1,100 to 1,800 µg/L. However, the median TBA concentration for Region 9 was roughly 10 times larger than Regions 4, 7, and 8 and as high as 125 times larger as the median TBA concentrations in other Regions. The observed statistical distributions of TBA concentrations show the concentrations vary widely among different Regions, with 90th percentile TBA concentrations in Region 4, 6, and 9 exceeding TBA concentrations in other Regions by as much as 40%. Excluding Region 9, Southern California (Region 4) had one of the highest statistical distributions for TBA concentration. The maximum TBA data shows that the NL of 12 µg/L was exceeded in 95% of sites by the end of 2019.



1

2

Figure 3-3. Summary of Surveys of TBA Concentrations in Groundwater

Figure 3-4 represents plot of cumulative percentile of site maximum TBA concentration in Southern California (Region 4) during 2019. A Comparison of median TBA concentration (1,200 µg/L) in Region 4 depicted in Table 1 with the NL of TBA (12 µg/L) demonstrates a 100 times difference. Even though these exceedances are currently not enforceable by the SWRCB due to lack of an MCL for TBA, one cannot overlook the potential magnitude of the impact of TBA hazard on California's groundwater resources.

The frequency distribution of TBA in Region 4 (Los Angeles County) and Region 9 (San Diego County) of California shows that approximately 6% of sites in these areas have at least one well with concentrations of TBA greater than 110,000 µg/L. In the data set reported by Shih et al., (2004) for Los Angeles, California, 5% of sites had TBA concentrations greater than 97,000 µg/L. A concentration of 110,000 µg/L would have to be diluted 10,000 fold to meet NL of 12 µg/L.

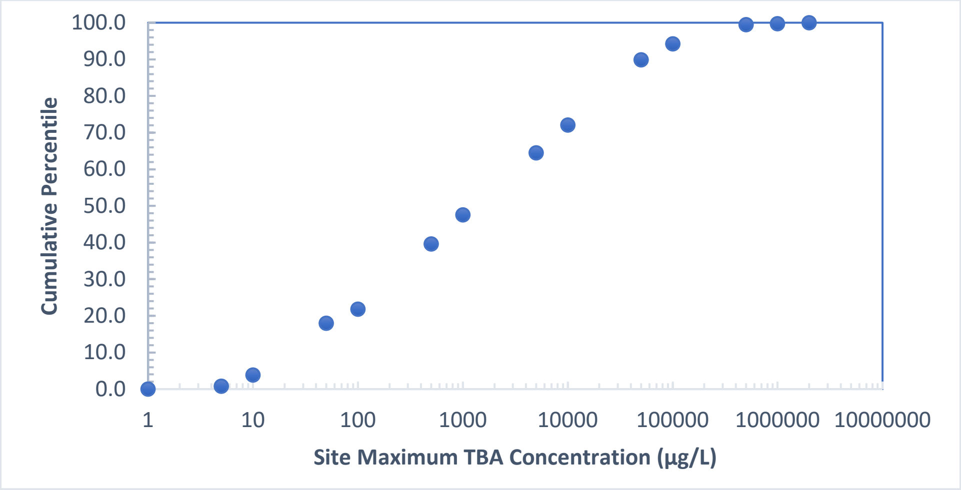


Figure 3-4. Plot of Cumulative Percentile of Site Maximum TBA Concentration in Groundwater within Region 4 Jurisdiction During 2019

The "Low Threat Closure Policy" adopted by the SWRCB, which is a tool to evaluate LUST sites in California for closure, does not mention TBA nor does it require regulators to consider TBA contamination in soil or groundwater in their closure review. This should be revisited based upon the toxicity data for TBA.

Fate and Transport

The National Center for Biotechnology Information describes TBA “a volatile, flammable, and colorless liquid at room temperature with a camphor-like odor which is fully miscible with water” (National Center for Biotechnology Information, PubChem Compound Database, CID=6386). TBA contains a tertiary butyl group and an alcohol (-OH) group attached to the central (tertiary) carbon. The persistence of TBA in water is associated with its high water solubility and low Henry’s Constant (Clark, 2001). Figure 3-5 shows the chemical structure of TBA, and Table 3-2 presents the chemical and physical properties of TBA.

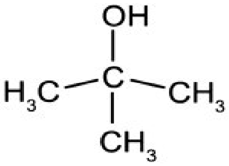


Figure 3-5. Structural Formula of TBA

Table 3-2. Chemical and Physical Properties of TBA (Clark, 2001)

Property	Value	Unit
Formula	$(CH_3)_3COH$	
Molar Mass	0.0741	kg/mol
Melting Point	298.85	K
Boiling Point	355.56	K
Specific Gravity (293 K)	0.786	
Density (293 K)	790	Kg/m^3
Aqueous Solubility (293 K)	Soluble	
Vapor Pressure (298 K)	5.6	KPa
Solubility in Gasoline	Miscible	
Log K_{ow}	0.35	
Log K_{oc}	1.57	
Henry’s Law Constant (298 K)	51.0	$(m^3)(Pa)/(mol)$
Flash Point	284.25	K
Odor	Camphor-like	
Odor Threshold in Air	0.000142-0.00182	Kg/m^3

LUSTs or pipelines can leak fuel containing TBA into the subsurface. Despite its relatively low vapor pressure, TBA can potentially volatilize into the gas phase, and the amount of the volatilization is inversely proportional to infiltration rate and soil moisture, and directly proportional to surface temperature (Clark, 2001). The fate of TBA in the atmosphere can be described via three processes (Zogorsky et al., 1996): 1) Atmospheric rainout of TBA in rainwater; 2) Photo-oxidation of TBA; and 3) Reaction of TBA with nitrogen monoxide (NO). Due to its low vapor pressure, TBA will tend to partition into atmospheric water. Rainout of TBA is likely to be significant for TBA releases in air. TBA primarily exists as a vapor in the ambient atmosphere or dissolved in water (Clark, 2001).

Competing chemical reactions in air are slow. A half-life of 34.5 hours is reported (Dilling et al., 1976) based on the reaction of TBA with NO. The half-life for the reaction of vapor phase TBA with photo-chemically generated hydroxyl radicals was estimated by EPA to be 1.09 months (Howard, 1995). Other sources estimated the half-life of TBA degradation by hydroxyl radicals of about 14 days (NIH, 2007).

However, since TBA tends to transfer to percolating soil water, a fuel leak containing TBA into the subsurface will eventually reach the groundwater (Clark, 2001). Due to its low organic carbon to water partitioning coefficient (Koc = 1.57; Table 3-2), adsorption onto soil organic matter will be insignificant (Zhuang et al., 2005). TBA has a low tendency to attach to the solids in the aquifer (Wilson and Adair, 2007).

Once in the groundwater, the TBA dissolved plume will be expected to travel faster than BTEX plume. Due to Bio-attenuation, the BTEX plume will eventually stabilize or biodegrade. However, TBA does not biodegrade as well as BTEX. Therefore, the TBA plume will continue to travel with groundwater and can end up as a groundwater contaminant (Zhuang et al., 2005).

Although pure TBA is soluble in water (Table 3-2), Raoult's Law predicts that the solubility of TBA will be reduced when mixed with gasoline. In addition, lower permeability soil, such as clays and silts, can hinder contaminant plume's movement. Dispersion in the groundwater flow, therefore, can be the cause of reduction of TBA concentration in the groundwater (Wilson and Adair, 2007).

Biodegradation in Subsurface

- **Anaerobic Biodegradation**

  Bacteria can grow on TBA. Biodegradation processes can occur under aerobic or anaerobic conditions. Schmidt et al., (2004) calculated the free energy yield for biodegradation of TBA with oxygen, nitrate, sulfate, or Iron (III) as electron acceptors and for the fermentation of TBA to methane. Based on the negative value for all free energies and the thermodynamics of the reactions, biodegradation of TBA should be theoretically possible under aerobic and anaerobic (nitrate, sulfate, Iron (III), and methanogenic) conditions (Wilson and Adair, 2007). Aerobic and nitrate reducing conditions released much more energy compared to iron and sulfate reduction, and methanogenesis. This means that biodegradation of TBA in sediment may be quicker in the presence of oxygen or nitrate. In the absence of oxygen or nitrate, TBA would require either sulfate, Iron (III), or Manganese (IV) in groundwater to biodegrade. Based on available literature, sulfate ions are not abundant in the groundwater of most LUST sites. Also, in areas of high TBA concentration, dissolved oxygen is limited in the groundwater (Wilson and Adair, 2007). According to Schmidt et al., (2004), unlike MTBE, TBA does not biodegrade in significant extent under methanogenic conditions.

  Although TBA is released along with MTBE into the groundwater during a gasoline spill, a major portion of the detected TBA in the dissolved phase is likely a product of biodegradation of the dissolved MTBE. Any available oxygen, nitrate, or sulfate in the groundwater are likely used up by other spilled petroleum constituents, such as the BTEX compounds leaving insufficient concentrations of the electron acceptors required for TBA biodegradation.

Different electron acceptors can dominate different areas of the aquifer (Finneran and Lovley, 2003; Wiedemeier et al., 1999). During a gasoline spill, oxygen is depleted first, followed by nitrate, sulfate, and finally methane. Therefore, it is reasonable to assume that the groundwater immediately adjacent to a gasoline spill is often methanogenic. The groundwater in the expanded region is then assumed to be sulfate reducing, followed by an iron (III)-reducing and nitrate reducing region. However, all electron accepting processes can occur at the same time as presented in Figure 6 (Wilson and Adair, 2007).

Others (API, 2012) have reported that acetogens, the CO_2-utilizing anaerobic microorganisms that generate acetic acid (CH_3COOH), are important in anaerobic biodegradation of MTBE (API, 2012). Acetogens use the methyl group ($-CH_3$) of MTBE as their electron donor and CO_2 as their electron acceptor to produce acetic acid and TBA as shown in equation 1. Fermentation of BTEX compounds can generate hydrogen gas which supports the process. Mackay et al. (2007) has identified this process as an abiotic hydrogenation reaction supported by biologically produced hydrogen (Mackay et al., 2007).

$$\underbrace{(CH_3)_3COCH_3}_{\text{MTBE}} + CO_2 + H_2 \xrightarrow{Acetogens} \underbrace{(CH_3)_3COH}_{\text{TBA}} + \underbrace{CH_3COOH}_{\text{Acetic Acid}} \qquad \text{Equation 3-1}$$

Despite theoretical considerations associated with TBA degradation under anaerobic conditions, Wilson and Adair (2007) still deem the fate of anaerobic TBA doubtful (Wilson and Adair, 2007). Others (Suflita, 1993) have referred to TBA's branched structure (tertiary alcohol) which resists microbial attack as a factor that further inhibits its degradation (Suflita, 1993). In the absence of oxygen, the half-life of TBA in soil has been estimated to be approximately 200 days (NIH, 2007).

Monitoring from 2004 through 2009 at Vandenberg Air Force Base (VAFB) Site 60 (a former service station on VAFB, Lompoc, CA) whose groundwater was under naturally sulfate-reducing conditions, revealed that no considerable degradation for TBA took place (Chakraborty, 2011). Also, laboratory studies showed that anaerobic degradation of TBA in VAFB Site 60 sediments did not occur at TBA concentrations of less than 2,000 micrograms per liter (Chakraborty, 2011). Some bench scale studies have shown that TBA resists degradation in sulfate-reducing and methanogenic environments (Bradley et al., 2002). Hikman (Hikman, 1989) stated that anaerobic degradation of TBA was extremely dependent on the initial dissolved concentration and the native microbial environment in the aquifer (Hikman, 1989). Others have also indicated that anaerobic biodegradation of TBA is slow, and that anaerobic conditions usually exist at LUST sites (Wiedemeier et al., 1995; Wiedemeier et al., 1999; Wilson and Adair, 2007). Thus, TBA accumulates during anaerobic biodegradation of MTBE (Wilson and Adair, 2007), and it is a persistent contaminant at LUST sites (Kolhatkar et al., 2000; Shih et al., 2004).

- **Aerobic Biodegradation**

Aerobic decomposition of MTBE can also produce TBA. It has been suggested (API 2012) that one oxygen atom from O_2 is first added onto the carbon of the methyl group in MTBE generating an unstable intermediate. This intermediate then decomposes to generate TBA. Co-metabolism by bacteria supported by alkane components of gasoline has also been suggested to have the potential of biodegrading both MTBE and TBA (API 2012).

The biodegradation of MTBE and TBA under aerobic conditions has been investigated via in situ and ex-situ bioremediation techniques. For example, use of bio-barriers to inject oxygen into the subsurface has been shown to be effective for degrading large dissolved plumes of MTBE. Biodegradation of TBA has also been investigated via in situ and ex-situ approaches (API, 2012).

In laboratory studies on sediments from two sites in South Carolina (Bradley et al., 1999) and sediments from VAFB Site 60, CA, indigenous bacteria were able to degrade TBA under aerobic conditions while oxygen was diffused into the groundwater (Mackay et al., 2001; Wilson et al., 2002). The bacterium detected in the study was very similar to bacterium Methylibium petroleiphilum strain PM1 (Hristova et al., 2003). Strain PM1 can degrade MTBE and TBA in the presence of sufficient oxygen (Hanson et al., 1999; Deeb et al., 2000). There are other bacteria that can also aerobically degrade MTBE and TBA, such as IFP2012 (Francois et al., 2002), and ENV735 (Hatzinger et al., 2001). Other aerobic mixed cultures produced from activated sludge (Salanitro et al., 1994; Eweis et al., 1997; Hanson et al., 1999; Francois et al., 2002), or from environmental samples (Fortin et al., 2001) have also been reported to be able to degrade MTBE and TBA. A bacterium (Strains KR1 and YZ1) from a granular activated carbon unit in a bicarbonate-buffered freshwater medium capable of degrading TBA has also been produced (Reinauer et al., 2008).

However, scaling these methods and develop them into technologies to use in the field could be practically problematic. According to EPA (EPA Guide, 2017), when adding bacteria into the subsurface, microbial growth or mineral precipitation can plug the injection wells and/or infiltration galleries. Another issue is creating aerobic conditions in the subsurface. Addition of oxygen to promote aerobic bioremediation by injecting air into the aquifer (air sparging) or using devices to slowly release oxygen (Johnson et al., 2003) may cause plume migration in the groundwater. In addition, preferential pathways may direct oxygen only in more permeable layer or channels within the aquifer (EPA Guide, 2017). On-ground structural restrictions or deep groundwater could make installations of wells at close spacing impossible or costly. (North et al., 2012).

Passive bioremediation, on the other hand, can be more economical as the native bacteria break down TBA. This process is slow and may not be practical when sensitive receptors, such as drinking water wells are at risk (EPA Guide, 2017).

Ex-situ treatment of TBA has been attempted via development of various aerobic bioreactor configurations (API, 2012). The presence of BTEX compounds has been reported to negatively impact bioremediation of TBA. Sedron et al., (2002) reported that in their batch remediation reactor, BTEX did not have a noticeable effect on MTBE degradation but slowed the TBA degradation (Sedron et al., 2002).

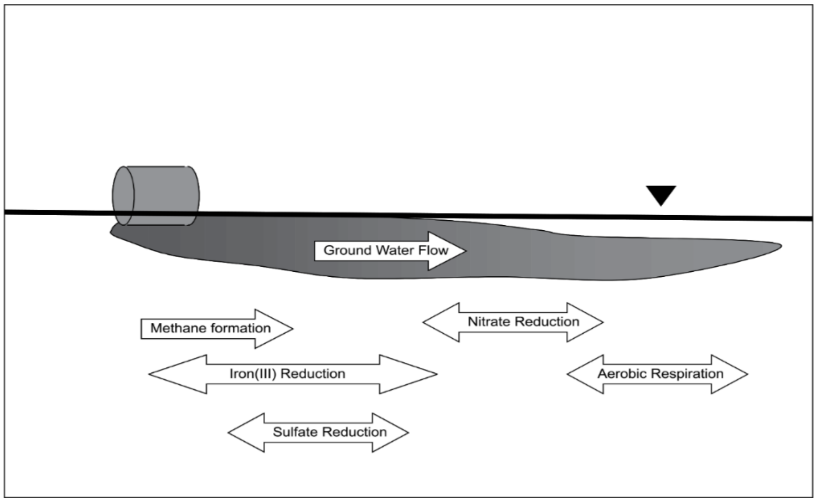


Figure 3-6. General distribution of terminal electron accepting processes in groundwater downgradient from a spill of gasoline (Adapted from Wilson and Adair, 2007)

In summary, the fate of TBA in soil and groundwater indicates biotransformation processes that form TBA and stability of TBA. Thus, California closure of LUST sites should be revisited, and a regulatory requirement should be considered for TBA contamination in soil and/or groundwater in closure reviews.

Conclusions

TBA is one of oxygenates that was used to enhance gasoline combustion. It was banned in early 2000. Yet, there are hundreds of confirmed cases of TBA contaminated groundwater throughout California. Although the use of TBA in gasoline has been banned for almost twenty years, TBA dissolved plume remains in the groundwater in many California LUST sites and threatens drinking water resources. Petroleum releases at LUSTs sites and MTBE biodegradation appear to be two primary sources of TBA in the environment.

TBA has been found in groundwater throughout California in alarmingly high concentrations. For example, during 2019, TBA was detected in the groundwater of Los Angeles County at concentrations as high as 2,200,000 µg/L. The median TBA concentration for San Diego County, California was roughly 125 times that of some other California Regions. Los Angeles County also had one of the highest statistical distributions for TBA concentration in Groundwater. Approximately 6% of sites in San Diego and Los Angeles Counties had at least one well with concentrations of TBA greater than 110,000 µg/L. The NL for TBA is 12 µg/L. According to DDW, NLs are advisory in nature and not enforceable standards. DDW has set the response level for TBA at 1,200 µg/L. No MCL has been adopted for TBA. Approximately 50% of the LUST sites in Los Angeles County are located within 1-mile radius of a drinking water production well.

The wide range of industrial and household applications of TBA, such as solvents, plastics, cosmetics, food, perfumes, paper, and metal coating, raises concern about its potential human health effects.

TBA may be potentially carcinogenic to humans based on its confirmed carcinogenicity on animals. As one of the primary metabolites of MTBE and ETBE, TBA can be generated in the body through consuming water contaminated with MTBE or ETBE.

TBA is very persistent in water and resists most methods of removal from groundwater. Bioremediation has the potential to be the most viable treatment method. However, it has several limitations, and without sufficient dissolved oxygen in the aerobic environment or other electron acceptors in the anaerobic environment, bioremediation will not be very efficient at removing TBA. Therefore, more research is needed to find the best chemical and/or biochemical processes to decompose TBA in groundwater.

In Conclusion:

1. Despite numerous documented health hazards, TBA has not received sufficient attention from government agencies. The toxicological evaluation of TBA indicates significant human health concerns. Thus, based upon the toxicological evidence, an MCL should be considered for TBA in drinking water.
2. The “Low Threat Closure Policy” adopted by the SWRCB, which is a tool to evaluate LUST sites in California for closure, does not mention TBA nor does it require regulators to consider TBA contamination in soil or groundwater in their closure review. This should be revisited based upon the toxicity data for TBA.
3. The fate of TBA in soil and groundwater indicates the biotransformation to form TBA and stability of TBA. Thus, California closure of LUST sites should be revisited, and a regulatory requirement should be considered for TBA contamination in soil and/or groundwater in closure reviews.

References

Amberg A, Rosner E, Dekant W (2000) Biotransformation and kinetics of excretion of ethyl tert-butyl ether in rats and humans, Toxicol Sci. 53: 194-201.

American Petroleum Institute (API) (2012) Clean Water Bulletins, Bulletin 26, TBA Biodegradation

Bi EP, Haderlein SB, Schmidt TC. (2005) Sorption of methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) to synthetic resins. Water Research. 39(17):4164–4176. [PubMed: 16139865]

Bradley PM, Landmeyer JE, Chapelle FH (1999). Aerobic mineralization of MTBE and tert-butyl alcohol by stream-bed sediment microorganisms. Environmental Science & Technology. 33(11):1877–1879.

Bradley PM, Landmeyer JE, Chapelle FH (2002) TBA biodegradation in surface-water sediments under aerobic and anaerobic conditions. Environmental Science & Technology. 36(19):4087–4090. [PubMed: 12380079]

California Environmental Protection Agency, Office of Environmental Health Hazard Assessment (OEHHA) (1999), Expedited Evaluation of Risk Assessment for Tertiary Butyl Alcohol in Drinking Water. http://www.oehha.ca.gov/water/pals/tba.html. Accessed 27 December 2019

California Geotracker Database, http://geotracker.waterboards.ca.gov. Accessed 27 December 2019

California State Water Resources Control Board (2020), Division of Drinking Water https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/NotificationLevels.html. Accessed May 27, 2020

Chakraborty, I. PhD dissertation (2001) Environmental Engineering, University of California, Davis; Davis, California. Anaerobic degradation of tert-butyl alcohol, methyl tert-butyl ether and ethanol in the subsurface.

Clark, J. J. (2001) tert-Butyl Alcohol: Chemical Properties, Production and Use, Fate and Transport, Toxicology, and Detection in Groundwater and Regulatory Standards. Chapter 7, pp 92-106

Cronk G (2015), Bench Scale Treatability Study, JAG Consulting Group.

Deeb RA, Scow KM, Alvarez-Cohen L (2000) Aerobic MTBE biodegradation: an examination of past studies, current challenges and future research directions. Biodegradation. 11(2–3):171–186. [PubMed: 11440243]

DeVaull GE., Sun PT., Rhodes IAL., Walsh DF. (2003) Study of tert-butyl alcohol (TBA) at selected underground storage tank remediation project sites in Orange County, California - Final Report. Houston, Texas: Shell Global Solutions.

Dilling, W.L., et al. (1976) Environmental Science & Technology, 19:351-6.

Environmental Protection Agency (2017) Toxicological Review of tert-Butyl Alcohol.

EPA Guide (2017) How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites. A Guide for Corrective Action Plan Reviewers. Available at https://www.epa.gov/ust/how-evaluate-alternative-cleanup-technologies-underground-storage-tank-sites-guide-corrective

Eweis JB, Chang DPY, Schroeder ED, Scow K, Morton RL, Caballero RC (1997) Meeting the challenge of MTBE biodegradation. Air & Waste Management Association’s 90th Annual Meeting & Exhibition, Toronto, Ontario, Canada, AWMA, Washington, DC

Feris KP, Hristova K, Gebreyesus B, Mackay D, Scow KM (2004) A shallow BTEX and MTBE contaminated aquifer supports a diverse microbial community. Microb Ecol 48:589–600

Fiorenza S, Suarez MP, Rifai HS. (2002) MTBE in groundwater: Status and remediation. Journal of Environmental Engineering. 128(9):773–781.

Fortin NY, Morales M, Nakagawa Y, Focht DD, Deshusses MA (2001) Methyl tert-butyl ether (MTBE) degradation by a microbial consortium. Environ Microbiol 3(6):407–416

Francois A, Mathis H, Godefroy D, Piveteau P, Fayolle F, Monot F (2002) Biodegradation of methyl tert-butyl ether and other fuel oxygenates by a new strain, Mycobacterium austroafricanum IFP 2012. Appl Environ Microbiol 68(6):2754–2762

Hanson JR, Ackerman CE, Scow KM (1999) Biodegradation of methyl tert-butyl ether by a bacterial pure culture. Applied and Environmental Microbiology. 65(11):4788–4792. [PubMed:10543787]

Hatzinger P, McClay K, Vainberg S, Tugusheva M, Condee C, Steffan R (2001) Biodegradation of methyl tert-butyl ether by a pure bacterial culture. Appl Environ Microbiol 67(12):5601–5607

Hickman G.T., Novak J.T. (1989) Environmental Science and Technology 23:525-532.

Hong Jun-Yan, Wang Yong-Yu, Bondoc F. Y., Lee M, Yang C. S., Hu Wen-Yu, Pan J (1999) Metabolism of Methyl tert-butyl Ether and Other Gasoline Ethers by Human Liver Microsomes and Heterologously Expressed Human Cytochromes P450: Identification of CYP2A6 as a Major Catalyst, Toxicology and Applied Pharmacology 160: 43-48.

Howard P.H. (1995) Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Lewis Publishers.

Hristova K, Gebreyesus B, Mackay D, Scow KM (2006) Naturally occurring bacteria similar to the methyl tert-butyl ether (MTBE)-degrading strain PM1 are present in MTBE-contaminated groundwater. Applied and Environmental Microbiology. 2003; 69(5):2616–2623. [PubMed: 12732529] ICIS, Timeline: A Very Short History of MTBE in the US, ICIS Editorial https://www.icis.com/explore/resources/news/2006/07/05/1070674/timeline-a-very-short-history-of-mtbe-in-the-us/. Accessed 27 December 2019

ITRC (Interstate Technology & Regulatory Council) (2005) Overview of Groundwater Remediation Technologies for MTBE and TBA. Washington, D.C: Interstate Technology & Regulatory Council, MTBE and Other Fuel Oxygenates Team. Available at http://www.itrcweb.org/Documents/MTBE-1.pdf

Johnson PC, Miller K, Bruce CL (2003) In Situ Bioremediation of MTBE in Groundwater – Final Technical Report. Available at http://estcp.org/content/search?cqp=Standard&SearchText=mtbe&x=0&y=0

Kane S.R., Beller H.R., Legler T. C., Koester C. J., Pinkart H. C., Halden R. U., Happel A. M. (2001) Aerobic Biodegradation of Methyl tert-Butyl Ether by Aquifer Bacteria from Leaking Underground Storage Tank Sites, Applied and Environmental Microbiology 67:5824-5829, https://doi.org/10.1128/AEM.67.12.5824-5829.2001. Accessed 27 December 2019

Kolhatkar R., Wilson JT., Dunlap LE., (2000) Evaluating Natural Biodegradation of MTBE at multiple UST sites. Petroleum and Organic Chemicals in Ground Water: Prevention, Detection and Remediation Conference & Exposition; Anaheim, California. p. 32-49.

Li Ke, Hokanson D. R., Crittenden J.C., Trussell R.R., Minakata D. (2008) Evaluating UV/H2O2 processes for methyl tert-butyl ether and tertiary butyl alcohol removal: Effect of pretreatment options and light sources, Journal of Water Research 42:5045-5053

Lin, Z., J. T. Wilson, and D. D. Fine (2003) “Avoiding Hydrolysis of Fuel Ether Oxygenates during Static Headspace Analysis,” Environmental Science and Technology 37(21): 4994–5000.

Mackay D, De Sieyes N, Einarson M, Feris K, Pappas A, Wood I, Jacobson L, …, Scow, K (2007) Impact of Ethanol on the Natural Attenuation of MTBE in a Normally Sulfate-Reducing Aquifer, Environ. Sci. Technol 41:2015-2021

Mackay, DM, Scow, KM, Wood, IA, Battaglia, V, Zertuche, A, Feris, KP, Hristova, K, Naas, C, Wilson, RD (2004) Evaluation of in situ biodegradation of TAME and other oxygenates by native microbial communities: Final Report. American Petroleum Institute; Houston, TX.

Mackay DM, Wilson RD, Scow KM, Einarson MD, Fowler B, Wood IA (2001) In situ remediation of MTBE at Vandenberg Air Force Base, California. Contaminated Soil, Sediment, and Water. 43–46. Spring Special Issue.

National Center for Biotechnology Information. PubChem Compound Database; CID=6386, https://pubchem.ncbi.nlm.nih.gov/compound/6386. Accessed 27 December 2019

National Institutes of Health (2005) Hazardous Substances Databank, Toxicology Data Network (TOXNET). National Library of Medicine Available from: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB. Accessed 27 December 2019

National Institutes of Health (2007), Hazardous Substances Data Bank, National Library of Medicine, t-Butyl alcohol. Bethesda, MD

Nihlén A, Löf A, Johanson G (1998) Controlled ethyl tert-butyl ether (ETBE) exposure of male volunteers: I. Toxicokenetics. Toxicol Sci. 46: 1-10. http://dx.doi.org/10.1006/toxs.1998.2516. Accessed 27 December 2019

North K. P., Mackay D. M., Kayne J. S., Petersen D, Rasa E, Rastegarzadeh L, Holland R. B., Scow K. M. (2012) In Situ Biotreatment of TBA with Recirculation/Oxygenation. Journal of Ground Water Monitoring & Remediation. 32(3): 52–62.

O'Reilly, K. T., M. E. Moir, C. D. Taylor, C. A. Smith, and M. R. Hyman (2001) "Hydrolysis of tert-Butyl Methyl Ether (MTBE) in Dilute Aqueous Acid," Environmental Science and Technology 35(19): 3954–61.

Patty's Industrial Hygiene and Toxicology. 3rd Revised Edition. Clayton G, Clayton F, Eds. John Wiley & Sons: New York, NY, 1982, p 4587

Reinauer KM, Zhang Y, Yang X, Finneran KT (2008) Aerobic biodegradation of tert-butyl alcohol (TBA) by psychro- and thermo-tolerant cultures derived from granular activated carbon (GAC). Biodegradation 19:259–268

Richards Sarah Anne (1999) Removal of methyl ter-butyl ether (MTBE) over a solid acid catalyst (Unpublished Master's Thesis). Lehigh University, Bethlehem, Pennsylvania

Rong, Y and Kerfoot H. B., (2003) Much Ado: How Big Is the Problem of Hydrolysis of Methyl Tertiary Butyl Ether (MTBE) to Form Tertiary Butyl Alcohol (tBA)? Environmental Forensics, 4:239-243

Salanitro J, Dias L, Williams M, Wisniewski H (1994) Isolation of a bacterial culture that degrades methyl t-butyl ether. Appl Environ Microbiol 60(7):2593–2596

Schmidt TC, Schirmer M, Weiss H, Haderlein SB. (2004) Microbial degradation of methyl tert-butyl ether and tert-butyl alcohol in the subsurface. Journal of Contaminant Hydrology. 70(3–4):173–203. [PubMed: 15134874]

Sedran M. A., Pruden A., Wilson G. J., Suidan M. T., Venosa A. D., (2002) Effect of BTEX on Degradation of MTBE and TBA by Mixed Bacterial Consortium. Journal of Environmental Engineering, 128:9(830)

Shell Global Solutions (US) Inc. (2003). Study of Tert-Butyl Alcohol (TBA) at Selected Underground Storage Tank Remediation Project Sites in Orange County, California. Prepared for S. J. Daugherty, Orange County Health Care Agency, Santa Ana, Calif.

Shih T, Rong Y, Harmon T, Suffet M (2004) Evaluation of the Impact of Fuel Hydrocarbons and Oxygenates on Groundwater Resources, Environ. Sci. Technol 38:42-48

Suflita J.M., Mormile M.R. (1993) Environ. Sci. Technol 27(5)

Sutherlan J, Adams C, Kekobad J (2005) Treatability of Alternative Fuel Oxygenates Using Advanced Oxidation, Air Stripping, and Carbon Adsorption. J. Environ. Eng. 131(4): 623-631

The Hazardous Substances Data Bank, National Library of Medicine, Bethesda, Maryland. 1985.

Wilson JT. and Adair C., US EPA; (2007). Monitored Natural Attenuation of Tertiary Butyl Alcohol (TBA) in Ground Water at Gasoline Spill Sites. EPA/600/R-07/100. Available at www.epa.gov/nrmrl/pubs/600r07100/600R07100.pdf

Wilson J.T., Kolhatkar R, Kuder T, Philp P, Daugherty J (2005) Stable Isotope Analysis of MTBE to Evaluate the Source of TBA in Ground Water. Ground Water Monitoring & Remediation 25(4): 108-116

Wilson RD, Mackay DM, Scow KM (2002). In situ MTBE biodegradation supported by diffusive oxygen release. Environmental Science & Technology. 36(2):190–199. [PubMed: 11827053]

Wiedemeier, TH.; Miller, RN.; Wilson, JT (1995) Significance of anaerobic processes for the intrinsic bioremediation of fuel hydrocarbons. Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Groundwater -Prevention, Detection, and Remediation Conference; November 29 - December 1, 1995; Houston, TX.

Wiedemeier TH, Rifai HS, Wilson JT, Newell CJ (1999) Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface. New York: John Wiley and Sons, Inc.

Yeh C.K., Novak J.T. (1991) Proceedings of the API/NGWA 1991 Petroleum Hydrocarbons & Organic Compounds in Groundwater: Prevention, Detection & Remediation Conference, Houston, Texas.

Zhuang W, Tay J, Yi S, Tay S (2005) Microbial adaptation to biodegradation of tert-butyl alcohol in a sequencing batch reactor. J Biotechnol 114:45–53

Zogorski, J.; Morduchowitz, A.; Baehr, A.; Bauman, B.; Conrad, D.; Drew, R.; Korte, N.; Lapham, W.; Pankow, J.; Washington, E. (1996) Fuel Oxygenates and Water Quality: Current Understanding of Sources, Occurrence in Natural Waters, Environmental Behavior, Fate, and Significance. Prepared for the Interagency Oxygenated Fuel Assessment and Coordinated by the Office of Science and Technology Policy.

Chapter 4

Evaluation of Hazard of Dissolved Tertiary Butyl Alcohol (TBA) Plume from Closed Leaking Underground Storage Tank (LUST) Sites in the Greater Los Angeles Area

Table of Contents Page

Abstract

A comprehensive analysis of TBA contamination in the groundwater was conducted on closed LUSTs sites in Southern California for between 2016 and 2019. The analysis revealed that closing practices at LARWQCB should be more stringent towards TBA contamination. TBA is considered a non-regulated chemical by the California Health Department and lacks a maximum contaminant level (MCL) in California. Therefore, the current health-based level of 12 micrograms per liter (µg/L) for TBA in drinking water established by the California Health Department, called “notification level” (NL) or “action level", is solely “advisory” and not enforceable.

As high as 88% of LUST sites during 2018-2019 FY were closed with TBA higher than its NL remaining in the groundwater. Analysis of the maximum TBA concentrations in the groundwater at closure shows that 25% of the time, remaining TBA concentrations were higher than 2,300 µg/L during 2016-2017, higher than 7,600 µg/L during 2017-2018, and higher than 4,400 µg/L during 2018-2019.

The steady increase of more than 70% of the maximum TBA plume lengths from 649 feet in 2016 to 1,128 feet in 2019 raises questions on the LARWQCB’s policy on TBA contamination. Considering the proximity of drinking water wells to the LUST sites in California in general, this points to an increase risk of impact on the drinking water resources. TBA remained above 12 µg/L in a substantial percentage (70% in 2016-1017, 72% in 2017-2018, and 88% in 2018-2019 fiscal years) of closed LUST sites. Despite numerous documented health hazards, TBA has not received sufficient attention from government agencies. The toxicological evaluation of TBA indicates significant human health concerns. Thus, based upon the toxicological evidence, an MCL should be considered for TBA in drinking water.

Keywords: Tertiary Butyl Alcohol, Methyl Tertiary Butyl Ether, Underground Storage Tanks, Groundwater Contamination, Plume Length

Introduction and Background

Leaking Underground Storage (or Fuel) Tanks (LUSTs or LUFTs) are the primary sources of tertiary butyl alcohol (TBA)-contaminated groundwater. TBA, an antiknock fuel oxygenate, can leak within the fuel, quickly dissolve in water, and contaminate the groundwater during the refining, distribution, and storage of oxygenated fuels. It can also form readily by biodegradation of methyl tertiary butyl ether (MTBE) (Schmidt et al., 2004; DeVaull et al., 2003; API, 2012)**.** Despite numerous documented health hazards of TBA, it has not received sufficient attention from government agencies (Toumari & Suffet, 2020). The toxicological evaluation of TBA indicates significant human health concerns. Thus, a maximum contaminant level (MCL) should be considered for TBA in drinking water in California (Toumari & Suffet, 2020). TBA is considered a non-regulated chemical by the California Health Department. (SWRCB 2018). Therefore, the current health-based level for TBA in drinking water established by the California Health Department, called “notification level” (NL) or “action level", is solely “advisory” and not enforceable. Currently, an NL of 12 micrograms per liter (μg/L) has been assigned for TBA. The Division of Drinking Water of the State Water Research Control Board (SWRCB) confirms that “NLs are advisory in nature and not enforceable standards.” (SWRCB 2018).

TBA is added directly to fuels as octane booster (American Petroleum Institute (API), 2012). It is also added to fuels, as a small impurity, along with MTBE or Ethyl Tertiary Butyl Ether (ETBE) (Shell Global Solutions, 2003; ITRC, 2005). In addition, TBA is a biotransformation product of MTBE degradation (Schmidt et al., 2004; DeVaull et al., 2003; API, 2012). Anaerobic degradation rates of ranging from 0.0035/day to 0.00035/day (half-lives of 0.54 years to 5.4 years) were reported at hydrocarbon-contaminated sites (Chisala et al., 2004). At several LUST sites, the concentration of TBA in groundwater is far greater than what can be expected from TBA as the primary oxygenate in the spilled gasoline (Wilson and Adair, 2007). Based on the ratio of TBA to MTBE at gasoline LUST sites in Orange County, California, Wilson et al., (2005) showed how TBA occurring from biodegradation of MTBE could explain the concentrations of TBA at 85% of the sites evaluated.

The persistence and mobility of TBA in subsurface environment have contributed to its presence and frequent detection in groundwater plumes and community water systems. However, to date, the state of knowledge is still quite limited for TBA. There are virtually no data on the environmental behavior of TBA, due primarily to difficulties in delineating its extent in the environment. The extent and magnitude of TBA contamination in the United States remains unknown. It is imperative that the environmental impacts of TBA be properly assessed, since limited evidence available suggests it would pose groundwater contamination threats similar to MTBE, if used in similar percent by volume amounts (Shih, et al., 2004). This paper will evaluate the extent and magnitude of TBA contamination in Southern California.

Figure 4-1 shows a side-by-side comparison of the locations of LUSTs in California and the locations of public drinking water wells. The figure “strongly shows a high instance of proximity and highlights concern that TBA in gasoline from LUSTs will find its way into deeper drinking water aquifers” (Hristova et al., 2010).

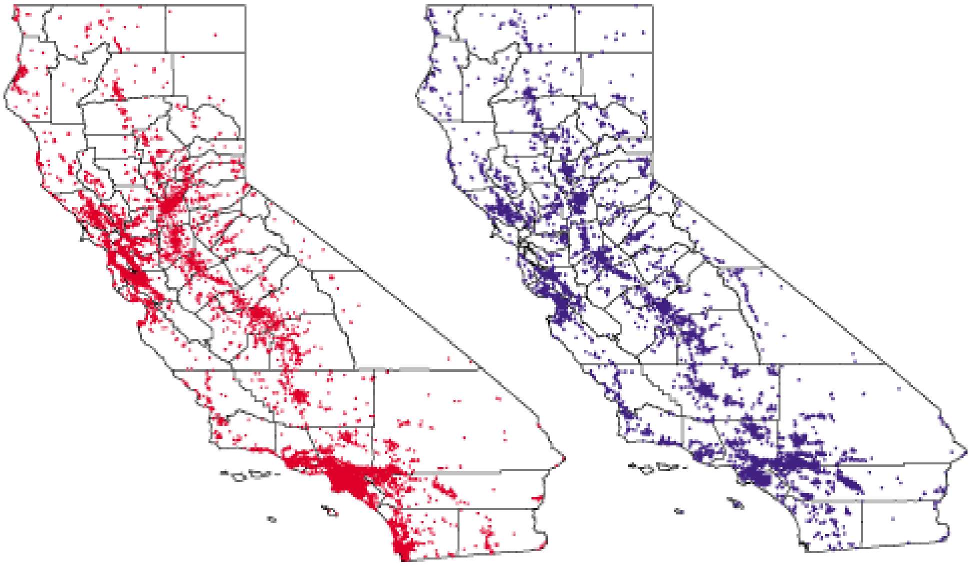


Figure 4-1. The locations of LUSTs in California (left) and the locations of public drinking water wells (right) (Hristova et al., 2010).

Objective

The objective of this paper is to characterize the potential for groundwater contamination of TBA by examining its occurrence, distribution, and extent at LUST sites in Southern California. Specifically, data on the frequency of detection, maximum concentration, and contaminant plume length in groundwater of TBA at LUST sites in the greater Los Angeles region are presented. Contaminant plume length is the primary measure in this research because it reflects the potential of the contaminant to impact drinking water wells. Analysis of these data will provide information on the current extent/magnitude of impact to groundwater resources caused by TBA releases and provides a basis for the California Division of Drinking Water of SWRCB to consider adopting an MCL for TBA. LUST sites are particularly important because they represent major point sources of gasoline constituents and the leading cause of oxygenate groundwater contamination (Shih, 2004). An extensive search of Geotracker revealed that in LUST sites overseen by the Los Angeles Regional

Water Quality Control Board (LARWQCB) alone, which comprises Los Angeles, Ventura counties, and portions of Kern and Santa Barbara counties, some 8,770 known releases of gasoline have already occurred by the end of 2018. Approximately 50% of the LUST sites in LARWQCB are located within 1-mile radius of a drinking water production well.

Evaluation of Occurrence, Distribution, and Extent of TBA in the Los Angeles Region

- **Los Angeles Regional Water Quality Control Board (LARWQCB) Case Closure Procedure**

The process for groundwater TBA data collection uses the groundwater monitoring reports (monitoring report) submitted to LARWQCB by the environmental consulting forms who perform monitoring and sampling of groundwater monitoring wells at LUST sites. Sampling and monitoring groundwater monitoring wells are generally conducted on a semi-annual basis according to the regulations set forth by the LARWQCB. Closure of LUST sites is determined primarily using the established procedures by the California State Water Resources Control Board's Low-Threat Closure Policy (LTCP, 2005).

- **Low Threat Closure Policy (LTCP)**

The Low Threat Closure Policy (LTCP) was developed by the SWRCB in 2005. The LTCP is a state policy for water quality control and applies to all petroleum LUST sites subject to Chapter 6.7 of Division 20 of the Health and Safety Code and Chapter 16 of Division 3 of Title 23 of the California Code of Regulations (H&S 2019). According to SWRCB, the purpose of this policy is to establish consistent statewide case closure criteria for low-threat petroleum UST sites. The policy seeks to increase LUST cleanup process efficiency in order to preserve the limited resources available for mitigation of releases posing a greater threat to human and environmental health. However, only certain petroleum constituents as described below have been considered by the LTCP to be harmful to human and environmental health. TBA is not included in this list. The complete LTCP document can be found at:

https://www.waterboards.ca.gov/board_decisions/adopted_orders/resolutions/2012/rs2012_0016atta.pdf.

The LTCP is comprised of the two main criteria:

1. General Criteria
2. Media Specific Criteria

The LTCP sets limits for the following parameters as determinant factors in closing LUST sites.

- Distance to drinking water wells
- Absence, stability, or removal to the maximum practicable extent of light non-aqueous phase liquid (LNAPL or free product)
- Total Petroleum Hydrocarbons as gasoline and diesel (TPHg, TPHd), Benzene, Ethylbenzene, MTBE, Naphthalene, and Poly-aromatic Hydrocarbons (PAHs)

Appendix A presents the details of the LTCP and describes the step-by-step approach required of the regulators to evaluate LUST sites for closure.

- **Evaluation Approach**

1. Using SWRCB Geotracker SWRCB's Geotracker Database (http://geotracker.waterboards.ca.gov), the total number of LUST cases in Greater Los Angeles Area closed during the past three years (2017 to 2019) were collected.
2. The maximum TBA concentrations for all of the above closed cases at the time of closure were obtained.
3. The concentration data were analyzed to evaluate the number of wells containing TBA concentrations at the time of closure.
4. The "Domenico Model" (Tong & Rong 2013) was used to calculate the TBA plume length based on the TBA concentration in the source and the in the downgradient wells.
5. The site conceptual model was analyzed to identify the groundwater gradient, the source well,

and the down-gradient wells to determine lateral delineation of the TBA plume.

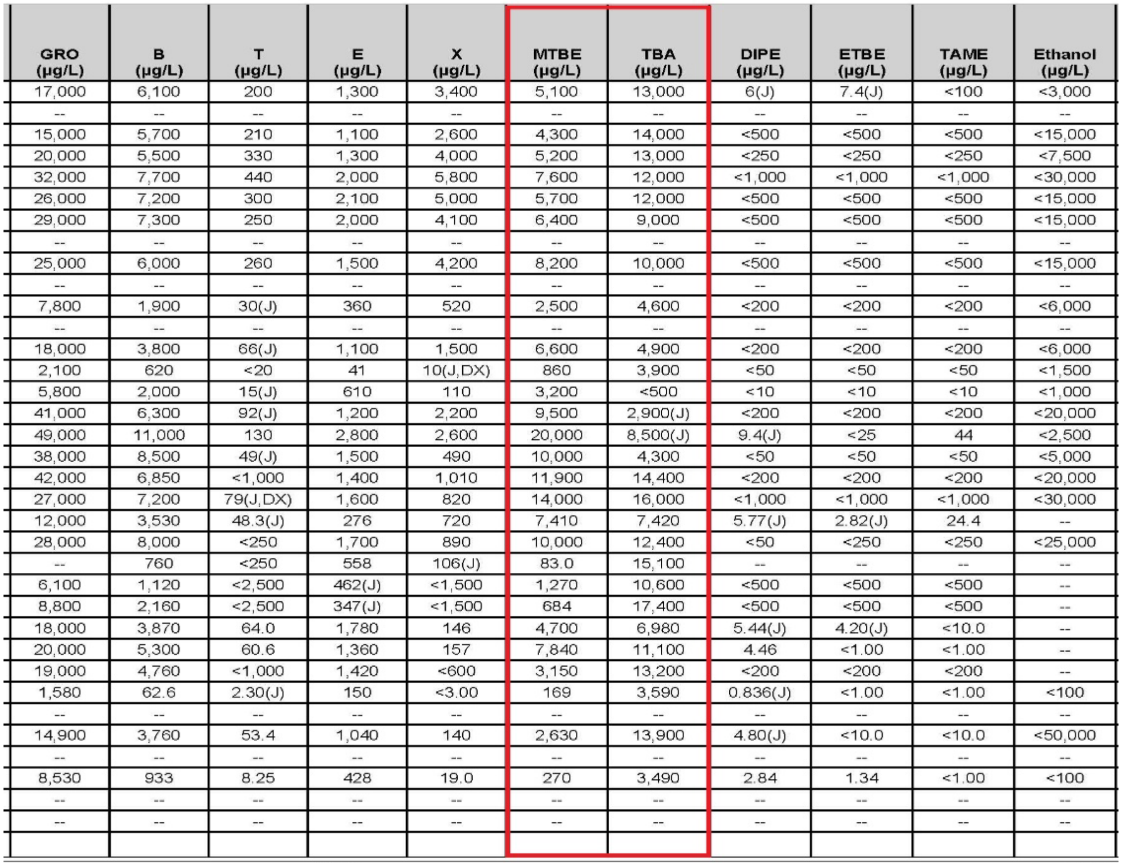
6. Statistical analyses were conducted on the above data as follows to achieve a consensus on the closure practices of the LARWQCB related to TBA.

- **Method of Analysis for Evaluation of TBA Data at Each Closed LUST site**

  1. TBA concentrations

     Analyze the monitoring report to find the maximum and historical TBA concentrations at the time of closure (Table 4-1).

Table 4-1: Current and Historical TBA Concentrations in Groundwater



GRO (µg/L)	B (µg/L)	T (µg/L)	E (µg/L)	X (µg/L)	MTBE (µg/L)	TBA (µg/L)	DIPE (µg/L)	ETBE (µg/L)	TAME (µg/L)	Ethanol (µg/L)
17,000	6,100	200	1,300	3,400	5,100	13,000	6(J)	7.4(J)	<100	<3,000
--	--	--	--	--	--	--	--	--	--	--
15,000	5,700	210	1,100	2,600	4,300	14,000	<500	<500	<500	<15,000
20,000	5,500	330	1,300	4,000	5,200	13,000	<250	<250	<250	<7,500
32,000	7,700	440	2,000	5,800	7,600	12,000	<1,000	<1,000	<1,000	<30,000
26,000	7,200	300	2,100	5,000	5,700	12,000	<500	<500	<500	<15,000
29,000	7,300	250	2,000	4,100	6,400	9,000	<500	<500	<500	<15,000
--	--	--	--	--	--	--	--	--	--	--
25,000	6,000	260	1,500	4,200	8,200	10,000	<500	<500	<500	<15,000
--	--	--	--	--	--	--	--	--	--	--
7,800	1,900	30(J)	360	520	2,500	4,600	<200	<200	<200	<6,000
--	--	--	--	--	--	--	--	--	--	--
18,000	3,800	66(J)	1,100	1,500	6,600	4,900	<200	<200	<200	<6,000
2,100	620	<20	41	10(J,DX)	860	3,900	<50	<50	<50	<1,500
5,800	2,000	15(J)	610	110	3,200	<500	<10	<10	<10	<1,000
41,000	6,300	92(J)	1,200	2,200	9,500	2,900(J)	<200	<200	<200	<20,000
49,000	11,000	130	2,800	2,600	20,000	8,500(J)	9.4(J)	<25	44	<2,500
38,000	8,500	49(J)	1,500	490	10,000	4,300	<50	<50	<50	<5,000
42,000	6,850	<1,000	1,400	1,010	11,900	14,400	<200	<200	<200	<20,000
27,000	7,200	79(J,DX)	1,600	820	14,000	16,000	<1,000	<1,000	<1,000	<30,000
12,000	3,530	48.3(J)	276	720	7,410	7,420	5.77(J)	2.82(J)	24.4	--
28,000	8,000	<250	1,700	890	10,000	12,400	<50	<250	<250	<25,000
--	760	<250	558	106(J)	83.0	15,100	--	--	--	--
6,100	1,120	<2,500	462(J)	<1,500	1,270	10,600	<500	<500	<500	--
8,800	2,160	<2,500	347(J)	<1,500	684	17,400	<500	<500	<500	--
18,000	3,870	64.0	1,780	146	4,700	6,980	5.44(J)	4.20(J)	<10.0	--
20,000	5,300	60.6	1,360	157	7,840	11,100	4.46	<1.00	<1.00	--
19,000	4,760	<1,000	1,420	<600	3,150	13,200	<200	<200	<200	--
1,580	62.6	2.30(J)	150	<3.00	169	3,590	0.836(J)	<1.00	<1.00	<100
--	--	--	--	--	--	--	--	--	--	--
14,900	3,760	53.4	1,040	140	2,630	13,900	4.80(J)	<10.0	<10.0	<50,000
--	--	--	--	--	--	--	--	--	--	--
8,530	933	8.25	428	19.0	270	3,490	2.84	1.34	<1.00	<100
--	--	--	--	--	--	--	--	--	--	--
--	--	--	--	--	--	--	--	--	--	--

  2. Plume Delineation

     Using the source well and groundwater flow direction, determine whether the TBA plume is delineated. The TBA plume is considered delineated if the TBA concentrations in the wells located in the direction of groundwater flow show a decreasing trend (Figures 4-2 and 4-3). As shown in Figure 4-3, the TBA concentration in the source well is 1,200 μg/L and the TBA concentration in the down-gradient well (GW-12) is 20.14 μg/L. Therefore, the TBA plume is considered delineated. There are cases where the groundwater flow direction is variable and the TBA plume is not fully delineated. For example, TBA may be delineated in the north and south directions but is not delineated in the east and west directions. For these scenarios, the cases are disregarded.

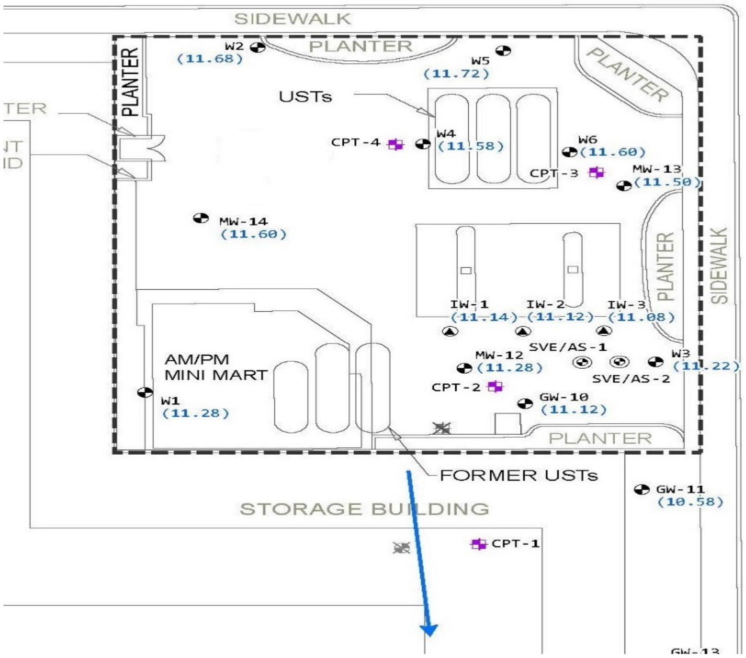


Figure 4-2. Groundwater Flow Gradient at a LUST site

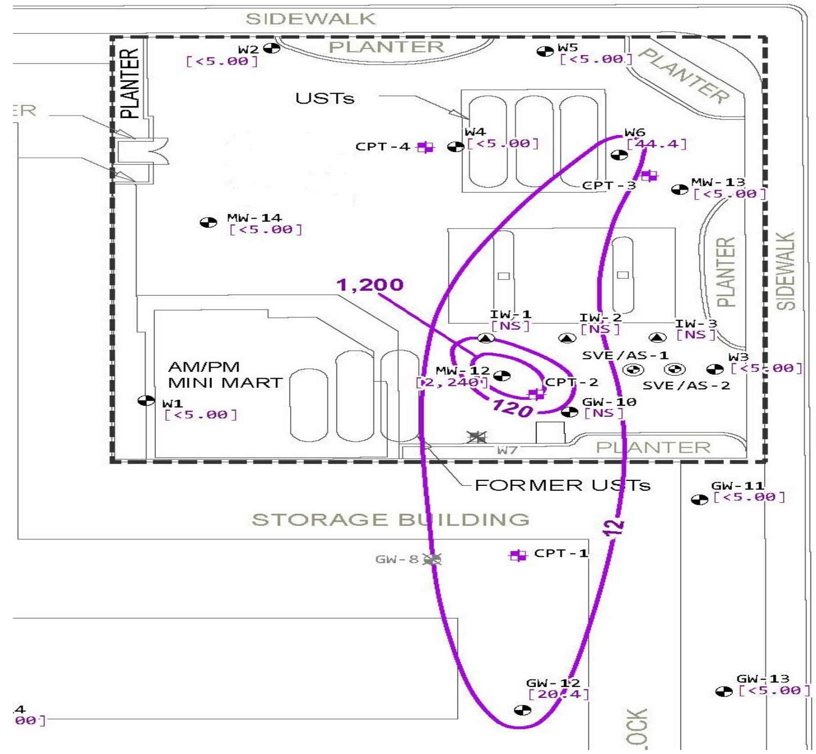


Figure 4-3: TBA Concentration Map

3. Plume Length

a. TBA Concentration Maps

If the provided TBA concentration map displays a contour of 12 μg/L, then the length of the 12 μg/L plume is measured in feet.

b. Domenico Model

If the TBA concentration map does not display a contour of 12 μg/L, the Domenico Spreadsheet Analytical Model Manual (Tong & Rong, 2013) is used. The Domenico analytical model is based on the advection-dispersion partial-differential equation for organic contaminant transport processes in groundwater as described below

(Domenico and Robbins 1985):

$$\frac{C_x}{C_0} = \exp\left\{ \frac{x}{2\alpha_x} \Bigg[1 - \left(1 + \frac{4\lambda\alpha_x}{\upsilon} \right)^{\frac{1}{2}} \Bigg] \Bigg] \right\} erf\left[\frac{Y}{4(\alpha_y x)^{\frac{1}{2}}} \right] erf\left[\frac{Z}{4(\alpha_z x)^{\frac{1}{2}}} \right] \quad \textbf{Equation 4-1}$$

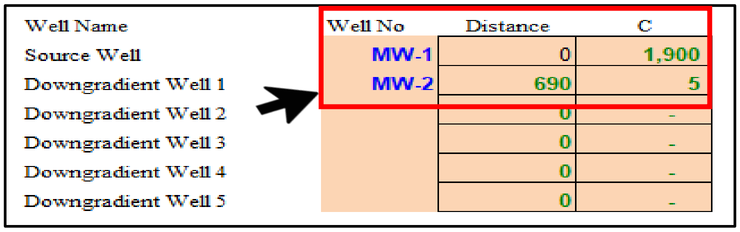
Where,
Cx = contaminant concentration in a downgradient well along the plume centerline at a distance *x* (mg/L),
C0 = contaminant concentration in the source well (mg/L),
x = centerline distance between the downgradient well and source well (ft),
αx, αy, and αz = longitudinal, transverse, and vertical dispersivity (ft), respectively,
Dx = αx.ν, Dy = αy.ν, Dz = αz.ν
λ = degradation rate constant (1/day),
λ = 0.693/t1/2 (where t1/2 is the degradation half-life of the compound).
ν = groundwater velocity (ft/day),
Y - source width (ft),
Z - source depth (ft),
erf - error function,
exp - exponential function.

Assumptions:
(1) The finite source dimension,
(2) The steady state source,
(3) Homogeneous aquifer properties,
(4) One dimensional groundwater flow,
(5) First order degradation rate,
(6) Contaminant concentration estimated at the centerline of the plume,
(7) Molecular diffusion based on concentration gradient is neglected,
(8) No retardation (e.g., sorption) in transport process.

1. Find the source well with the highest TBA concentration and one downgradient well with decreasing TBA concentrations along (or near) the centerline.
2. Measure the distance between the source well and the downgradient well (in feet).
3. Enter the distance and concentrations of the two wells in the first table of the Domenico Spreadsheet (Figure 4-4). If the downgradient well is not along the centerline, measure the off-center line angle as well as distance in feet.

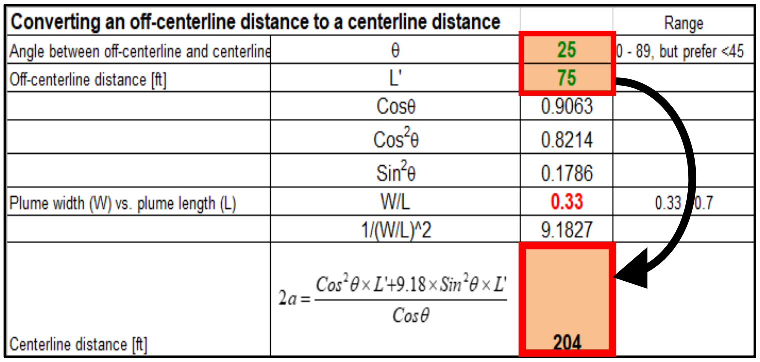
   i. Enter the information in the spreadsheet, and the centerline distance (ft) will be given (Figure 4-5).
   ii. Enter the given distance in the first table of the spreadsheet (Figure 4-4).

4. A model evaluation graph will then show the source well plotted with a linear line and the downgradient well.
5. Manipulate the longitudinal dispersivity of the aquifer (α_x), groundwater velocity (ν), and degradation rate constant (λ) within the allowable ranges (α_x: 0.35 – 4 ft, ν: 0.01 – 0.5 ft/day, λ: 0.1 – 0.001 day^{-1}) until the line passes both the source well and the downgradient well (Figure 4-6).
6. The distance to the source well from a plume boundary of 12 μg/L is given (Figure 4-7).



Well Name	Well No	Distance	C
Source Well	MW-1	0	1,900
Downgradient Well 1	MW-2	690	5
Downgradient Well 2		0	-
Downgradient Well 3		0	-
Downgradient Well 4		0	-
Downgradient Well 5		0	-

Figure 4-4: Distance and Concentration Inputs



Converting an off-centerline distance to a centerline distance			Range
Angle between off-centerline and centerline	θ	25	0 - 89, but prefer <45
Off-centerline distance [ft]	L'	75	
	Cosθ	0.9063	
	Cos^{2}θ	0.8214	
	Sin^{2}θ	0.1786	
Plume width (W) vs. plume length (L)	W/L	0.33	0.33 0.7
	1/(W/L)^2	9.1827	
Centerline distance [ft]	$2a = \frac{Cos^2\theta \times L' + 9.18 \times Sin^2\theta \times L'}{Cos\theta}$	204	

Figure 4-5. Off-Centerline Conversion to Centerline Distance

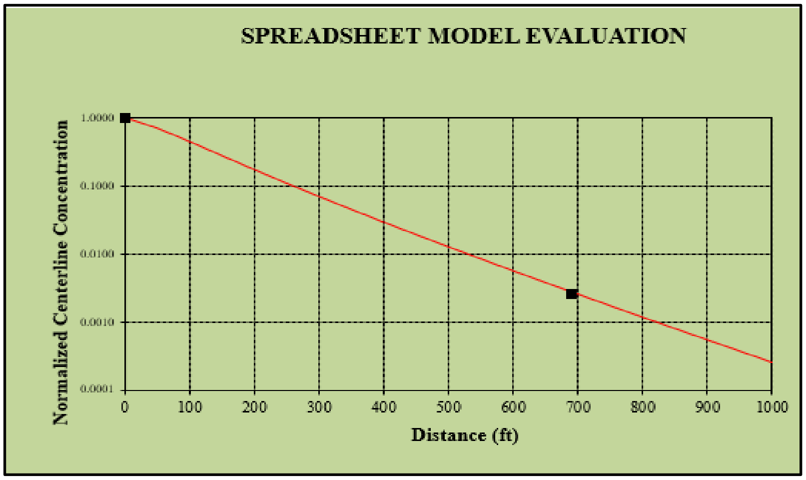
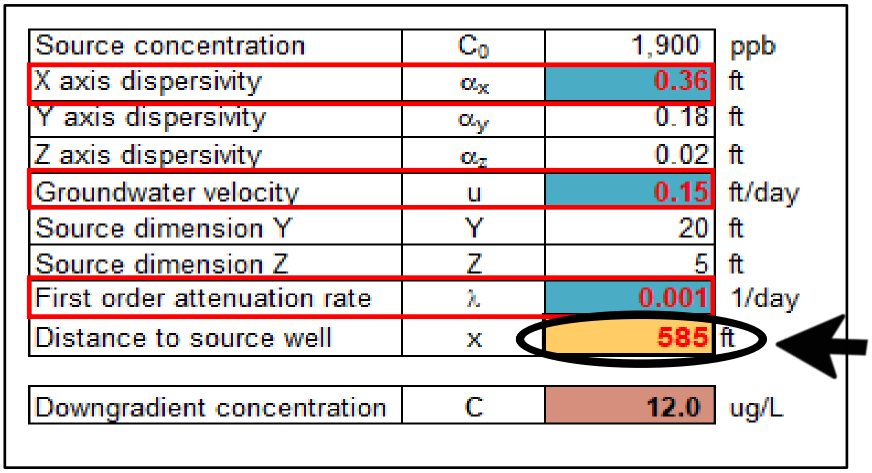


Figure 4-6: Spreadsheet Model Evaluation



Source concentration	C_0	1,900	ppb
X axis dispersivity	α_x	0.36	ft
Y axis dispersivity	α_y	0.18	ft
Z axis dispersivity	α_z	0.02	ft
Groundwater velocity	u	0.15	ft/day
Source dimension Y	Y	20	ft
Source dimension Z	Z	5	ft
First order attenuation rate	λ	0.001	1/day
Distance to source well	x	585	ft
Downgradient concentration	C	12.0	ug/L

Figure 4-7 Domenico Model Parameters

Results

A total of 263 LUST sites (sites) were closed from July 2016 till June 2019. Figure 4-8 shows the percentage of closed sites with TBA remaining in groundwater over a 3-year period. A total of 82 of these sites detected TBA higher than its NL (12 µg/L) at the time of closure.

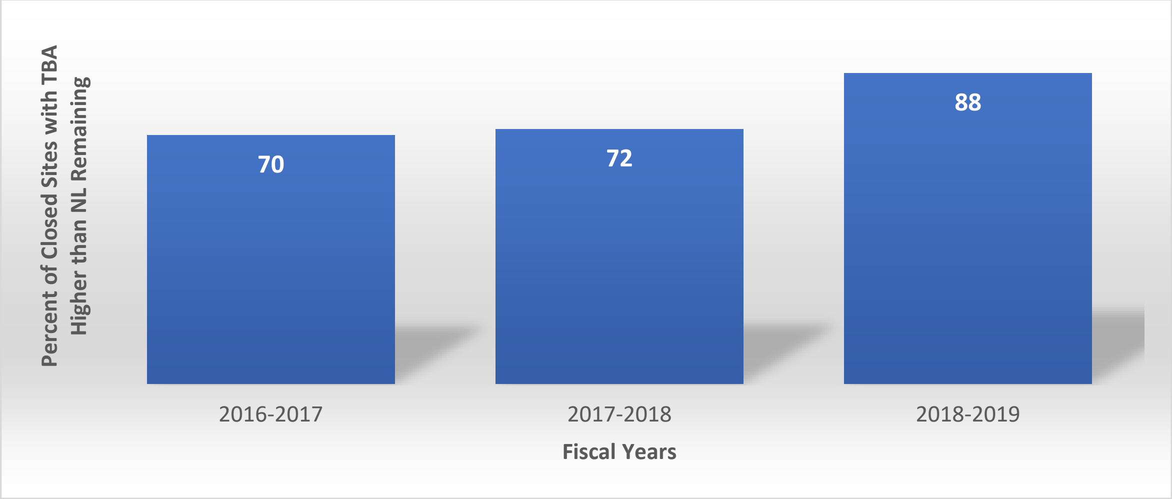


Figure 4-8. Percent of Closed Sites with TBA Remaining in Groundwater

The median TBA concentration between 2016 and 2019 in the sites located in Region 4 was 1,200 μg/L. This concentration, which is 100 times greater than the NL and equal to the response level for TBA was used as a residual "concentration index" at the sites in Region 4 at the time of closure in the specified date range.

Table 4-2 shows the number of groundwater monitoring wells that detected TBA at the specified ranges in each FY. Four categories were selected; less than 12 μg/L, between 12 and 60 μg/L, between 60 and 1,200 μg/L and larger than 1,200 μg/L. 60 μg/L was selected because it is 5 times the NL, and 1,200 μg/L was selected because it is the median of maximum TBA concentrations at closure of all sites. Figure 4-9 shows the percentage of groundwater monitoring wells with the specified TBA concentration ranges detected at closure.

Table 4-2. Total number of groundwater monitoring wells at closure with TBA (in μg/L)

	TBA<12	12< TBA< 60	60<TBA<1,200	TBA>1,200
FY 2016-2017	222	27	21	15
FY 2017-2018	300	43	47	42
FY 2018-2019	199	15	42	25
Total	721	85	110	82

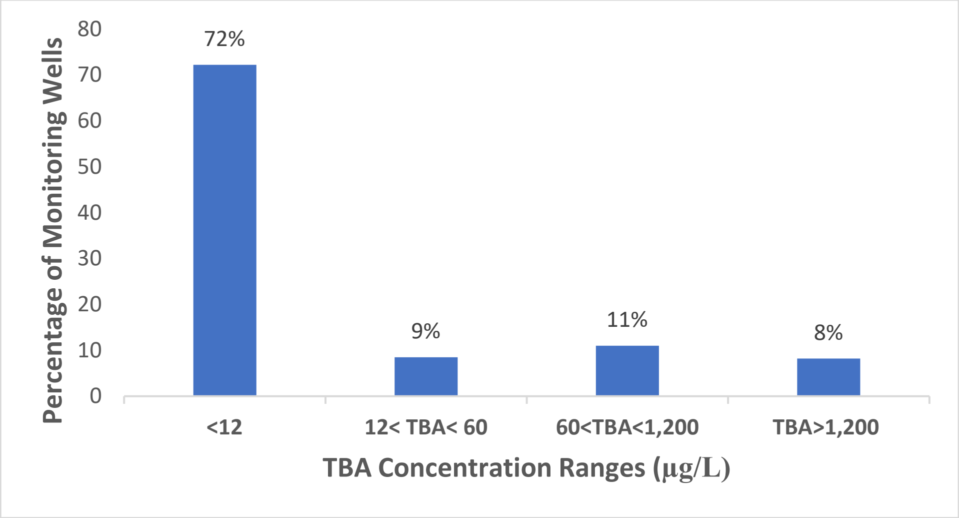
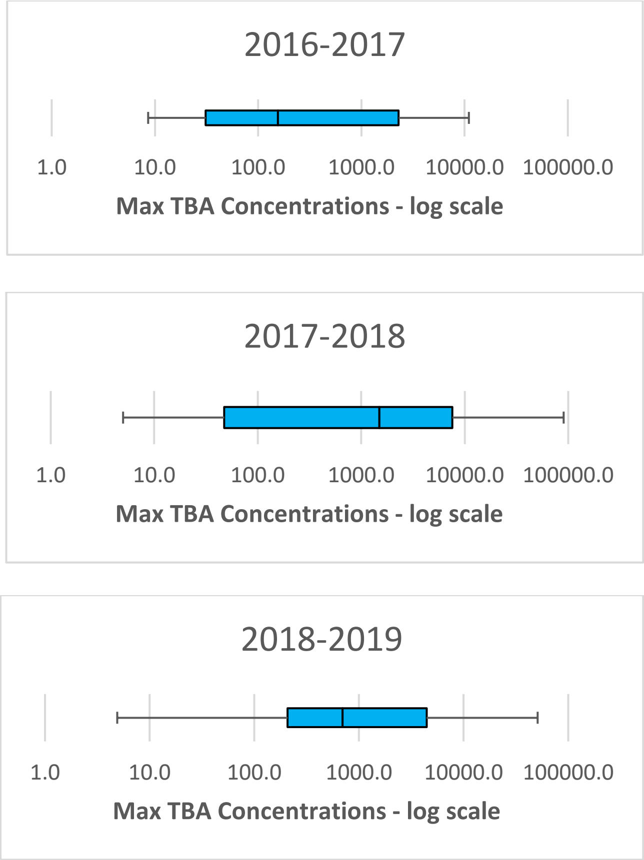


Figure 4-9. Percentage of Groundwater Monitoring Wells with the Specified TBA Concentration Ranges Detected at Closure

Figure 4-10 is a "box and whisker" plot in log scale showing the median, minimum, maximum, 25th percentile, and 75th percentile of maximum TBA concentrations detected at all sites at closure in each FY. Along with each plot, the actual statistical values were provided for reference. As shown in Figure 4-10, during 2016-2017, the median TBA concentration was 156 µg/L, and 25% of the time, TBA concentrations were higher than 2,300 µg/L. During 2017-2018, the median TBA concentration was 1,500 µg/L, and 25% of the time, TBA concentrations were higher than 7,600 µg/L. During 2018-2019, the median TBA concentration was 696.6 µg/L, and 25% of the time, TBA concentrations were higher than 4,434.3 µg/L.



25 Percentile	31
Median	156
75 Percentile	2,300
Minimum	8.6
maximum	11,000

25 Percentile	47.5
Median	1,500
75 Percentile	7,600
Minimum	5.0
maximum	90,300

25 Percentile	207.5
Median	696.6
75 Percentile	4,434.3
Minimum	4.9
maximum	51,000

Figure 4-10. Statistical Data of Maximum Groundwater TBA Concentrations at Closure

Plume Length

TBA plume delineation was conducted in 9 sites during the FY 2016-2017 with an average of 230.9 feet, 22 sites during the FY 2017-2018 with an average of 211.9 feet, and 20 sites during the FY 2018-2019 with an average length of 328.70 feet. The Domenico Model could not be utilized to calculate plume length for some of the sites for reasons, such as variable groundwater flow direction, lack of plume delineation, and lack of down-gradient groundwater monitoring wells. As shown in Table 4-3 and Figure 4-11, the maximum TBA plume lengths have continuously increased from 649 feet during the fiscal year 2016-2017 to 1,128 feet during the fiscal year 2018-2019. This is an alarming increase of more than 70% which raises questions regarding the Los Angeles Regional Water Board's shift towards a more loosening policy on TBA contamination.

Table 4-3. TBA Plume Length Calculated by the Domenico Model

	TBA Plume Length (ft)		
	FY 2016-2017	FY 2017-2018	FY 2018-2019
Minimum	57	25	21
Maximum	649	712	1,128
Average	230.9	211.9	328.7

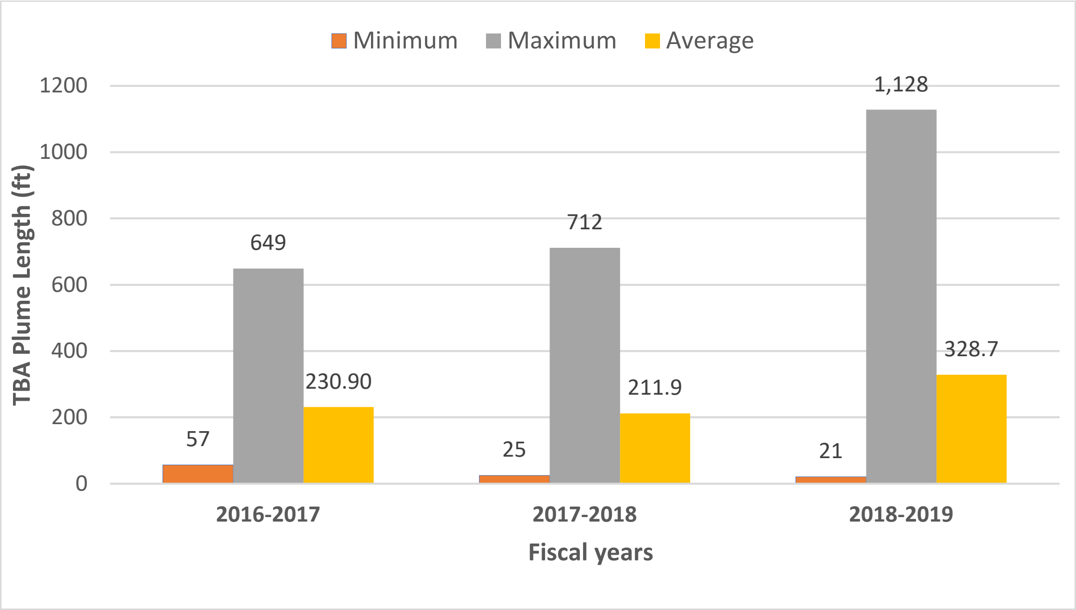


Figure 4-11. TBA Plume Length Calculated by the Domenico Model

The assumptions made by (Tong & Rong, 2013) in the Domenico Model to simplify calculations of plume lengths do not always reflect the reality of the subsurface conditions, and therefore should not be ignored. In most LUST sites, a leak takes place over a period of time, and then it stops as the entire content is released or the tank is removed. Meanwhile, the soil can become the secondary source and "feed" the groundwater contamination. Depending on the lithology of the subsurface, such secondary source may or may not be considered to be releasing the fuel at steady state. Also, aquifer properties are almost never homogeneous. In addition, the one-dimensional assumption of groundwater flow is dependent on the homogeneity of the aquifer. As mentioned before, the degradation of TBA is slow especially under the naturally anaerobic environment of the subsurface at LUST sites. It is also heavily dependent on the characteristics of the microbial community of the site. Therefore, assuming a first-order degradation rate may not be always accurate.

A search of the Groundwater Ambient Monitoring and Assessment (GAMA) system created by the SWRCB in 2000 (GAMA, 2020) revealed that during the three years from 2016 through 2019, TBA concentration in wells installed to monitor for landfill leachate in Southern California (Region 4) exceeded its NL 22 times. The maximum TBA concentration reported 360 μg/L and the median concentration was 210 μg/L.

TBA Concentration Reduction:

The percent TBA concentration reduction for the cases where at least one of the above methods were employed was calculated as follows:

$$\%\text{Reduction} = \frac{\text{Historical Max Concentration} - \text{Max Concentration at Closure}}{\text{Historical Maximum Concentration}} \times 100\%$$

Equation 4-2

Table 4-4 and Figure 4-12 show the concentration reduction values and trends for the specified fiscal years.

Table 4-4. The TBA concentration reduction values for the past three years in closed cases

TBA Concentration Reduction (%)	Number of Closed Cases		
	FY 2016-2017	FY 2017-2018	FY 2018-2019
>90	20	33	22
50-90	4	9	5
<50	6	4	5

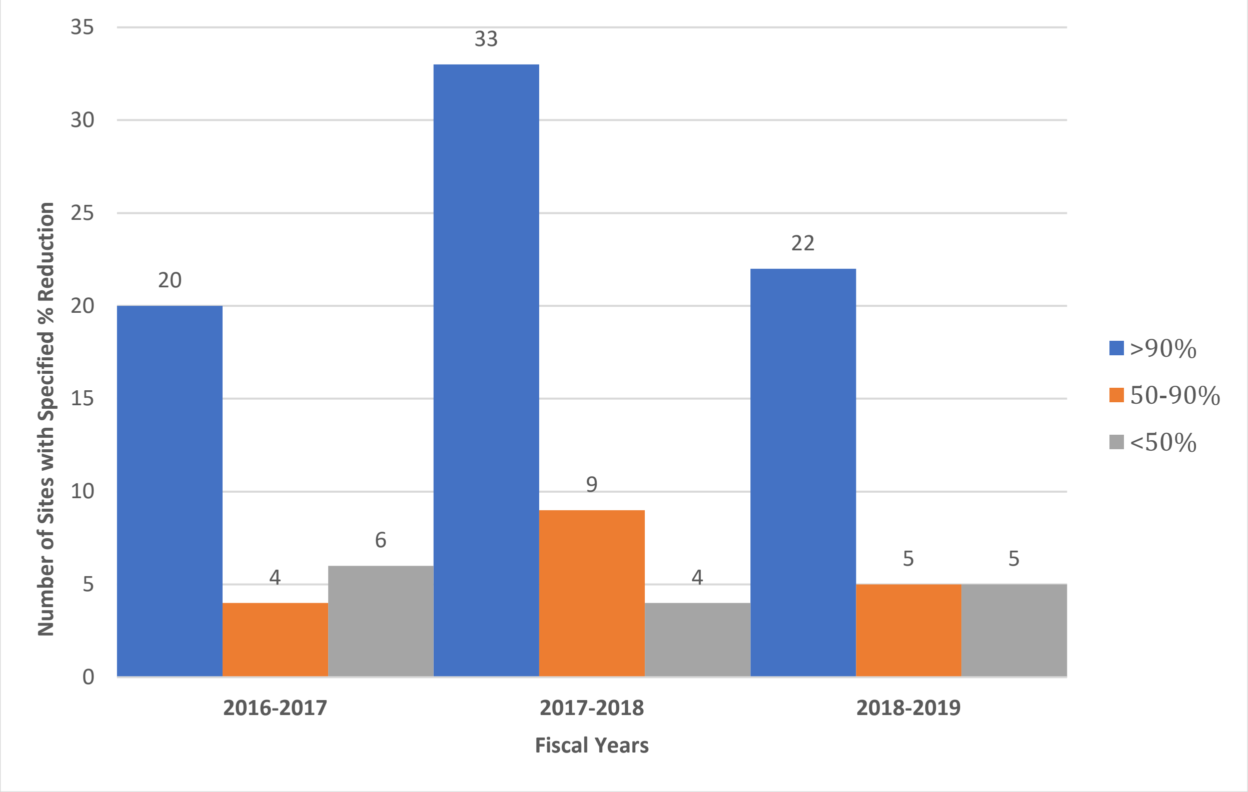


Figure 4-12. TBA Concentration Reduction (%) at Case Closure

As Figure 4-13 shows, a TBA concentration reduction of greater than 90% occurred in most cases regardless of the year. Such reduction can be the result of a combination of natural degradation and implementation of one or more of the above mentioned methods. Despite such a large reduction, TBA concentrations of greater than the NL remained in the groundwater in as high as 88% of the cases. These numbers show that routine remedial measures that have historically been used at LUST sites are generally inefficient in reducing TBA concentrations to below safe levels.

Conclusions

- Closing practices at LARWQCB should be more stringent towards TBA contamination. As high as 88% of LUST sites during 2018-2019 FY were closed with TBA higher than its NL remaining in the groundwater. Analysis of the maximum TBA concentrations in the groundwater at closure shows that 25% of the time, remaining TBA concentrations were higher than 2,300 µg/L during 2016-2017, higher than 7,600 µg/L during 2017-2018, and higher than 4,400 µg/L during 2018-2019.

- The steady increase of the maximum TBA plume lengths from 649 feet during the fiscal year 2016-2017 to 1,128 feet during the fiscal year 2018-2019 is concerning. This is an alarming increase of more than 70% which raises questions on whether such increase is random, or whether it could reflect the LARWQCB's shift towards a more loosening policy on TBA contamination. Considering the proximity of drinking water wells to the LUST sites in California in general, this points to an increase risk of impact on the drinking water resources.
- A combination of the routine and conventional groundwater remedial methods were able to reduce TBA concentrations in groundwater by as much as 90%. However, TBA remained at concentrations above 12 µg/L, in as high as 88% of these cases.
- A research work of systematic comparison between the TBA concentrations measured in the field and those calculated using the simplified Domenico Model should be conducted to assess the degree of accuracy of the model employed in this paper and in the closure practices of California regulators in general.
- The data obtained from analyzing groundwater monitoring wells show that about 72% of the wells detected TBA concentrations of lower than 12 µg/L. While this is a positive outcome, one cannot ignore the fact that about 28% of the 998 wells investigated which amounts to 279 wells detected TBA at higher than 12 µg/L over three years. Considering the tendency of TBA to dissolve in groundwater and move with the groundwater flow; the slow natural degradation of TBA; and the close proximity of the drinking water wells to the vast number of groundwater monitoring wells installed at LUST sites in Southern California, the potential threat to drinking water sources at some point in the future is real.

References

American Petroleum Institute (API) (2012) Clean Water Bulletins, Bulletin 26, TBA Biodegradation

American Petroleum Institute (API) (1996). A Guide to the Assessment and Remediation of Underground Petroleum Releases. Publication 1628, 3rd Edition.

ASTM International (2006). Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface. E2531-06.

California Health & Safety Code Statutes of Chapter 6.7, Underground Storage of Hazardous Substances (2019). Available at https://www.waterboards.ca.gov/ust/regulatory/docs/hsc_6_7_01_2019.pdf

California State Water Resources Control Board (2018), Division of Drinking Water https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/NotificationLevels.html. Accessed 27 December 2019

California Water Resources Control Board, Low-Threat Underground Storage Tank Case Closure Policy (LTCP) (2005) Available at https://www.waterboards.ca.gov/board_decisions/adopted_orders/resolutions/2012/rs2012_0016atta.pdf.

California Water Resources Control Board, Division of Water Quality, Groundwater Ambient Monitoring & Assessment Program (GAMA), 2020 available at https://www.waterboards.ca.gov/water_issues/programs/gama/about.html

Chisala, B.N., N.G. Tait, and D.N. Lerner (2004). Evaluating the risk of methyl tertiary-butyl ether (MTBE) to urban groundwater. *Hydrology: Science and Practice for the 21st Century.* Volume II: 243-249.

Day, M.J. (2001). The fate and transport of oxygenates and other petroleum constituents, and their influence on appropriate underground storage tank management. Contaminated Soil Sediment and Water. August. pp. 14-19.

DeVaull GE., Sun PT., Rhodes IAL., Walsh DF. (2003) Study of tert-butyl alcohol (TBA) at selected underground storage tank remediation project sites in Orange County, California - Final Report. Houston, Texas: Shell Global Solutions.

Domenico, P.A. (1987), An analytical model for multidimensional transport of a decaying contaminant species, *Journal of Hydrology*, Vol. 91, 49-58.

EPA Guide (2017) How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites. A Guide for Corrective Action Plan Reviewers. Available at https://www.epa.gov/ust/how-evaluate-alternative-cleanup-technologies-underground-storage-tank-sites-guide-corrective

Hawai'i Department of Health (HDOH) Hazard Evaluation and Emergency Response (HEER) Office Technical Guidance Manual (TGM), 2018 available at https://health.hawaii.gov/heer/files/2019/11/TGM-LNAPL_Final-7-30-2018_posted.pdf

Hristova, K; Hicks, K; Schmidt, R; and Scow, K (2010) National Institute of Environmental Health Sciences, Superfund Research Program, MTBE and TBA Cleanup-New Research Perspectives

Interstate Technology & Regulatory Council (2009). Evaluating LNAPL Remedial Technologies for Achieving Project Goals.

Li Ke, Hokanson D. R., Crittenden J.C., Trussell R.R., Minakata D. (2008) Evaluating UV/H_2O_2 processes for methyl tert-butyl ether and tertiary butyl alcohol removal: Effect of pretreatment options and light sources, Journal of Water Research 42:5045-5053

Los Angeles Regional Water Quality Control Board, Underground Storage Tank Program, https://www.waterboards.ca.gov/losangeles/water_issues/programs/ust

National Institutes of Health (2005) Hazardous Substances Databank, Toxicology Data Network (TOXNET). National Library of Medicine Available from: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB. Accessed 27 December 2019

Potter, T.L. and K.E. Simmons (1998). Composition of Petroleum Mixtures. Massachusetts: Amherst Scientific Publishers, Vol. 2.

Shih, T; Rong, Y; Harmon, T; Suffet, M. Evaluation of the Impact of Fuel Hydrocarbons and Oxygenates on Groundwater Resources, Environ. Sci. Technol., 2004, 38, 42-48

Schmidt TC, Schirmer M, Weiss H, Haderlein SB. (2004) Microbial degradation of methyl tert-butyl ether and tert-butyl alcohol in the subsurface. Journal of Contaminant Hydrology. 70(3–4):173–203. [PubMed: 15134874]

Tong W and Rong Y (2002). Estimation of Methyl tert-Butyl Ether Plume Length Using the Domenico Analytical Model. Journal of Environmental Forensics Vol 3: pp 81-87.

Tong, W and Rong, Y (2013) Domenico Spreadsheet Analytical Model Manual, Underground Storage Tank Section, California Regional Water Quality Control Board - Los Angeles Region, Los Angeles, CA

Toumari, A and Suffet, I. H. (Mel) (2020) Evaluation of Tertiary Butyl Alcohol (TBA) Impact on Groundwater: Application to California. University of California at Los Angeles, Environmental Science & Engineering Program, Institute of the Environment and Sustainability, School of Letters and Science, Los Angeles, CA

U.S. Environmental Protection Agency (EPA). 1995a. Light non-aqueous phase liquids. Ground Water Issue. EPA/540/S-95/500.

Chapter 5

Treatment Methods for Tertiary Butyl Alcohol (TBA) Removal at Leaking Underground Storage Tank (LUST) Sites in the Greater Los Angeles Area

Table of Contents Page

Abstract

Several groundwater remedial technologies were implemented during the three fiscal years from 2016 through 2019. In most cases, a combination of these methods were employed at each LUST site. Information on the remedial technologies employed for each site was collected and their effectiveness was evaluated by comparing the methods. Aerobic bioremediation appeared to be the most effective method of treating TBA contamination but was only employed at one case during the time investigated. The remedial methods were not nearly as effective in reducing the TBA concentrations as compared with the MTBE concentrations which indicated that reducing TBA to safe levels in the groundwater requires a more specific and targeted approach.

Keywords: Tertiary Butyl Alcohol, Methyl Tertiary Butyl Ether, Underground Storage Tanks, Groundwater Contamination, Groundwater Remediation

Introduction

According to Environmental Protection Agency's (EPA), as of September 2019, there are 546,192 active underground storage tanks (USTs) at 197,000 facilities nationwide. Also, more than 555,384 releases from leaking underground storage tanks (LUSTs) have been reported. Cleanups have been completed at 490,624 of these sites, and 64,760 sites still to be cleaned up. As of September 2019, there are 37,511 active USTs in California. There have been 44,733 confirmed releases and cleanup has been initiated for 43,853 of these cases. A total of 41,862 cleanups have been reported as completed (Performance Measures, 2020). Although the exact number was not reported, but a large percentage of these cases are expected to include groundwater contamination. Considering the only advisory and non-enforceable notification level (NL) of 12 μg/L (California State Water Resources Control Board (SWRCB), 2018) and the absence of an MCL in drinking water for tertiary butyl alcohol (TBA) in California, it is doubtful and concerning whether these cleanups included TBA treatment and reduction of concentrations to below the current NL.

Several groundwater remedial technologies were implemented at the LUST sites that were closed during the three fiscal years from 2016 through 2019 as follows.

- **Dual (Multi) Phase Extraction (DPE)/Pump and Treat/Groundwater Over-purge**

  Dual-phase extraction (DPE), also known as multi-phase extraction, vacuum-enhanced extraction, or bio-slurping, is an in-situ technology that uses pumps to remove various combinations of contaminated groundwater, separate-phase petroleum product, and hydrocarbon vapor from the subsurface. Extracted liquids and vapor are treated and collected for disposal, or re-injected to the subsurface (where permissible). DPE systems can be effective in removing separate-phase product from the subsurface, thereby reducing concentrations of petroleum hydrocarbons in both the saturated and unsaturated zones of the subsurface. DPE systems are typically designed to maximize extraction rates; however, the technology also stimulates biodegradation of petroleum constituents in the unsaturated zone by increasing the supply of oxygen (EPA 2017). However, biodegradation in the dissolved phase does not occur in this case. Therefore, the concern for TBA treatment using this method can be viewed in the context of ex-situ bioremediation, whose limitations have been discussed in Chapter 3 in detail.

- **Soil Vapor Extraction (SVE)**

Soil vapor extraction (SVE), also known as soil venting or vacuum extraction, is an in situ remedial technology that reduces concentrations of volatile constituents in petroleum products adsorbed to soils in the unsaturated (vadose) zone. In this technology, a vacuum is applied to the soil matrix to create a negative pressure gradient that causes movement of vapors toward extraction wells. Volatile constituents are readily removed from the subsurface through the extraction wells. The extracted vapors are then treated, as necessary, and discharged to the atmosphere or reinjected to the subsurface (where permissible). This technology has been proven effective in reducing concentrations of volatile organic compounds (VOCs) and certain semi-volatile organic compounds (SVOCs) found in petroleum products at underground storage tank (UST) sites. SVE is generally more successful when applied to the lighter (more volatile) petroleum products such as gasoline. Diesel fuel, heating oils, and kerosene, which are less volatile than gasoline, are not readily treated by SVE (EPA 2017).

SVE is considered inefficient for TBA removal from saturated zone as the applied vacuum is designed to remove contaminant from the soil matrix. This method is also inefficient for TBA removal from unsaturated zone as TBA’s low organic carbon to water partitioning coefficient (Koc = 1.57) inhibits TBA adsorption to soil. Therefore, a release of TBA-containing fuel into the subsurface will likely leave most of the TBA in the dissolved phase.

- **Air Sparging (AS)**

Air sparging (AS) is an in-situ remedial technology that reduces concentrations of volatile constituents in petroleum products that are adsorbed to soils and dissolved in groundwater. This technology, which is also known as "in situ air stripping" and "in situ volatilization," involves the injection of contaminant-free air into the subsurface saturated zone, enabling a phase transfer of hydrocarbons from a dissolved state to a vapor phase. The air is then vented through the unsaturated zone. AS is most often used together with soil vapor extraction (SVE), but it can also be used with other remedial technologies. When AS is combined with SVE, the SVE system creates a negative pressure in the unsaturated zone through a series of extraction wells to control the vapor plume migration. This combined system is called AS/SVE (EPA 2017).

This method is considered generally inefficient for TBA contaminated groundwater treatment as TBA's low Henry's Constant and high water solubility prevent TBA from easily partitioning from the dissolved phase into the gas phase by air stripping.

- **In-Situ Chemical Oxidation (Ozone/Hydrogen Peroxide/ Sodium Persulfate Injection)**

Petroleum contaminant decomposition and in-situ destruction may be accomplished using chemical oxidation technologies. In contrast to other remedial technologies, contaminant reduction can be seen in short time frames (e.g., weeks or months). A variety of chemical oxidants and application techniques can be used to bring oxidizing materials into contact with subsurface contaminants to remediate the contamination. With sufficient contact time with the organic contaminants, chemical oxidants may be capable of converting the petroleum hydrocarbon mass to carbon dioxide and water and ultimately irreversibly reduce concentrations of petroleum hydrocarbons in soil and groundwater. While many of the chemical oxidants have been used in wastewater treatment for decades, only recently have they been used to treat hydrocarbon-contaminated groundwater and soil in-situ.

Chemical oxidation technologies are predominantly used to address contaminants in the source area saturated zone and capillary fringe. Cost concerns can preclude the use of chemical oxidation technologies to address large and dilute petroleum contaminant plumes. More frequently, chemical oxidation technologies are employed to treat smaller source areas where the petroleum mass is more concentrated. However, where excessive petroleum contaminant mass exists in the source area and where there is a significant thickness of mobile non-aqueous phase liquids (NAPLs), other remedial technologies (e.g., free product recovery) may need to precede chemical oxidation for the remediation to be safe and cost-effective (EPA 2017).

Ozone O_3 injection can be beneficial in treating TBA partly because the oxygen generated as a result of the reaction of ozone with volatile organic compounds contaminant can promote biodegradation. As mentioned before, oxidation can be counterproductive as oxidation of MTBE-impacted groundwater can produce TBA. O_3/H_2O_2 can also be used to treat TBA. However, A big concern is the formation of bromate as byproduct, which is classified by the U.S. EPA as a ‘‘probable human carcinogen’’ and has a current drinking water limit of 10 μg/L (National Institutes of Health 2005). Although there are methods available to control bromate formation in O_3/H_2O_2 process, it would be cost prohibitive and difficult to consistently control the bromate below the regulatory limit because the concentration of bromide in the raw water can be as high as 900 μg/L (Li et al 2008).

- **Ex-Situ Chemical Oxidation**

Ex-situ chemical oxidation involves mixing an oxidizing compound with contaminated groundwater in a vessel (Delisle, 2019). The oxidizing agents most commonly used for the chemical treatment of organic contaminants are ozone, O_3/H_2O_2, UV/H_2O_2, chlorine, and sodium hypochlorite. The main advantage of ex-situ chemical oxidation as opposed to in-situ chemical oxidation is that it allows sufficient time for oxidation of TBA to occur in a controlled environment. As mentioned in in-situ chemical oxidation, incomplete oxidation or formation of intermediate contaminants may occur during TBA treatment. The process is also not cost-effective for high TBA concentrations because of the large amounts of oxidizing agent required. For example, when chlorine is used for oxidation, undesirable substitution products such as haloforms can form. Chemicals other than TBA may consume oxidizing agents, increasing treatment cost and creating the potential for forming undesirable byproducts.

Hydrogen peroxide oxidation reaction alone is not strong enough to completely degrade organic compounds. However, when mixed with UV light or ozone, hydroxy radicals are formed which is the true oxidizing agent. Hydroxy radicals are highly reactive and non-specific and can efficiently treat hydrocarbons. Chemical oxidation therefore occurs for all substances having oxidation potential, such as metals or organic compounds.

Ex-situ chemical oxidation has some general limitations:

- It is exothermic which can increase the volatilization, desorption, or biodegradation of contaminants.
- There is a potential for incomplete oxidation.
- It may be necessary to recover and treat the produced volatile compounds.
- Presence of compounds other than the contaminants to be treated may react with the oxidant reduce the efficiency of the technology.
- Costs can increase rapidly if large quantities of oxidants are required.
- Ex situ treatment costs may be higher than in situ treatment costs due to increased handling of the contaminated material.

- **Light Non-Aqueous Phase Liquid (LNAPL or Free Product) Removal**

  One-time LNAPL releases become stable incrementally, but generally over time frames of 10 years or less. The older the release, the more likely it is to be stable; (i.e., LNAPL is no longer spreading to a larger area or depth provided that hydrogeologic conditions do not change.) All things being equal, smaller releases stabilize more quickly than larger releases and spread a lesser distance. Lighter products, such as gasoline, travel farther and faster than heavy products. After a plume stabilizes, the remaining mass (free phase and residual) drives potential long-term risks as chemicals continue to slowly partition from the LNAPL into water and vapor. A significant portion of the dissolved phase TBA is contributed from direct dissolution of TBA-bearing LNAPL sources. Therefore, the longer the LNAPL remains, the more likely the contaminants like TBA will partition in the dissolved phase and spread.

- **Enhanced Biodegradation (Bioremediation)**

  Enhanced (active or in-situ) biodegradation adds bacteria to the subsurface to promote bio decay of TBA. Bioremediation currently is the most effective method of removing TBA from the dissolved phase. However, as discussed in detail in Chapter 3, degradation of MTBE to TBA is more favorable and may further increase the dissolved TBA concentration. Further degradation of TBA, which most likely occurs under anaerobic conditions, will have several limitations, will be slow, and will not be very efficient.

Objective

The objective of this paper is to evaluate the efficiency of groundwater remedial methods on reducing the TBA concentrations in groundwater below its NL. These remedial methods were employed at the LUST sites in the Greater Los Angeles area during the 2016 through 2019 fiscal years (FY). Analysis of these data will help identify the following:

- The methods, if any, that have been effective on TBA

- Technical limitations of the methods
- Recommendation to implement new approaches

Approach

Several groundwater remedial technologies were implemented at the LUST sites that were closed during the three fiscal years from 2016 through 2019. Please note that in most cases a combination of these methods were employed at each LUST site. Information on the remedial technologies was collected from the remediation summary section of the groundwater monitoring reports submitted by the environmental consulting firms. The number of cases for which any method(s) was/were employed was recorded. The effectiveness of these methods on reducing TBA concentrations in the groundwater was then evaluated by comparing the methods. The effectiveness of these remedial methods on treating methyl tertiary butyl ether (MTBE) was also evaluated and compared with TBA. MTBE biodegrades to form TBA in the subsurface and therefore, is considered an additional source of TBA in the groundwater in addition to the direct releases from the LUSTs.

Results

Table 5-1 shows the number of closed cases in which the specified groundwater remediation method was implemented. Please note that in most cases, a combination of these methods were employed in each LUST site. Figure 5-1 shows the general relative frequency of the employed methods.

Table 5-1. Number of Closed Cases with TBA Remediated between 2016 and 2019

Year	DPE	SVE	AS	Chemical Oxidation	LNAPL Removal	Bioremediation
2016-2017	18	13	9	0	2	0
2017-2018	21	23	2	9	2	1
2018-2019	25	19	9	11	1	0
Total	64	55	20	20	5	0

DPE = Dual (Multi) Phase Extraction/Pump & Treat/Groundwater Over-Purge
SVE = Soil Vapor Extraction
AS = Air Sparging
Chemical Oxidation = Subsurface Injection of Ozone/Hydrogen Peroxide/Sodium Peroxide/Oxygen

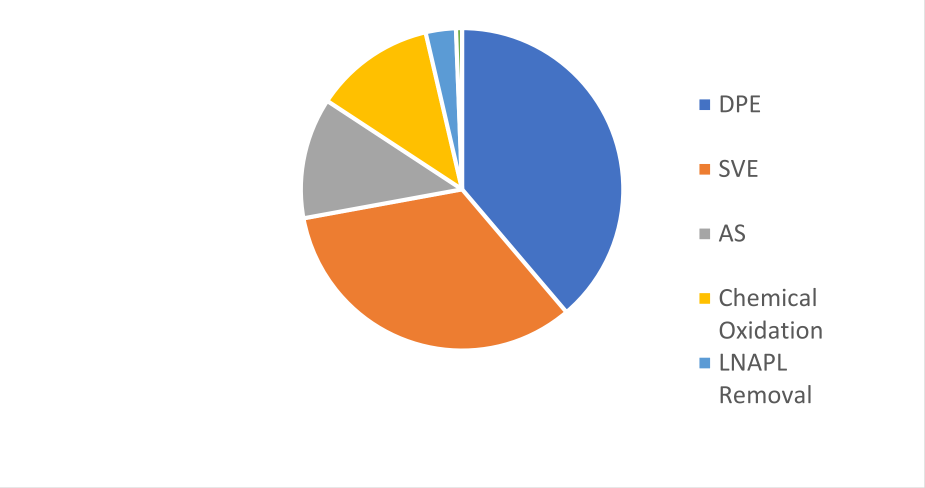
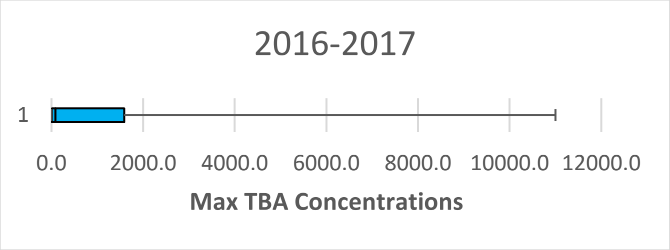


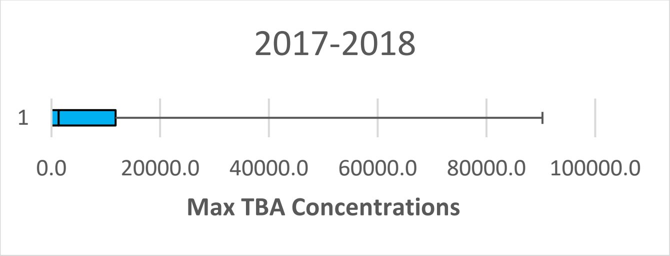
Figure 5-1. Total Remediation Technologies Implemented in TBA Cases Closed (2016 – 2019)

<u>Statistical Data for DPE</u>

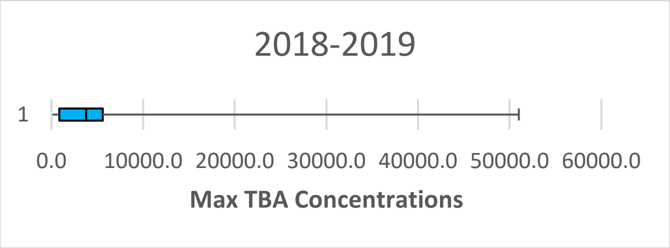
Figure 5-2 shows statistical analysis of the TBA concentrations remaining in closed LUST sites for which three main remedial methods (DPE, AS, and SVE) were implemented.



25 Percentile	6.5
Median	83
75 Percentile	1585
Minimum	0
maximum	11,000

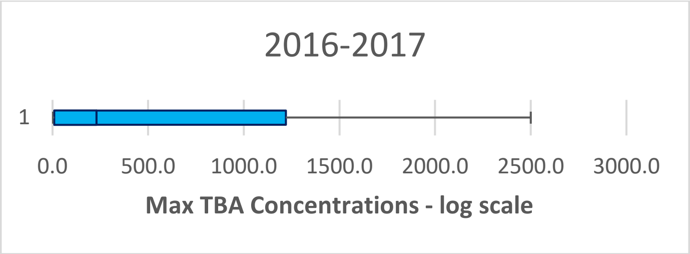


25 Percentile	0
Median	1300
75 Percentile	11775
Minimum	0
maximum	90,300

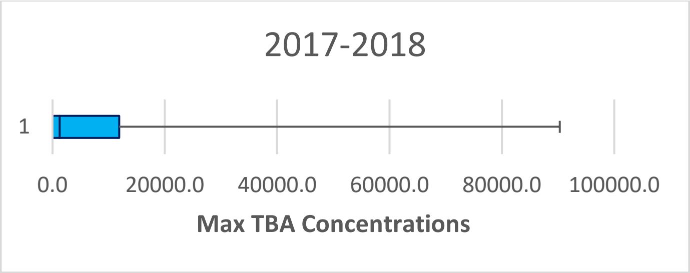


25 Percentile	864
Median	3800
75 Percentile	5586.3
Minimum	0
maximum	51,000

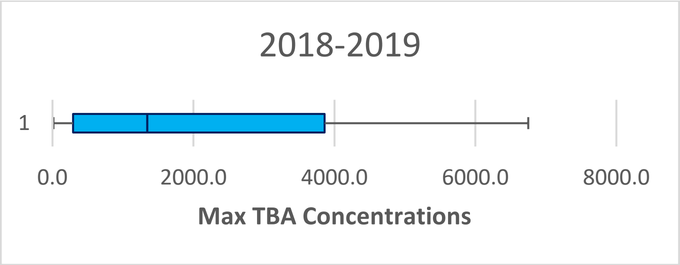
Statistical Data for AS



25 Percentile	9.0
Median	230
75 Percentile	1220
Minimum	0
maximum	2500

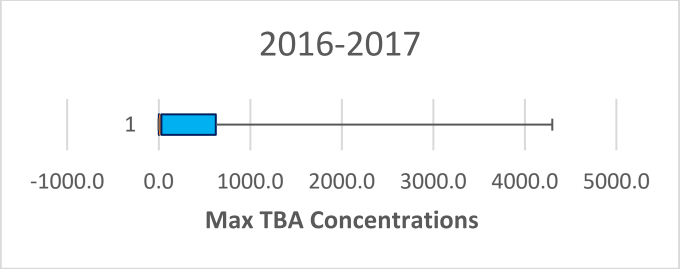


25 Percentile	5
Median	1250
75 Percentile	11850
Minimum	0
maximum	90300

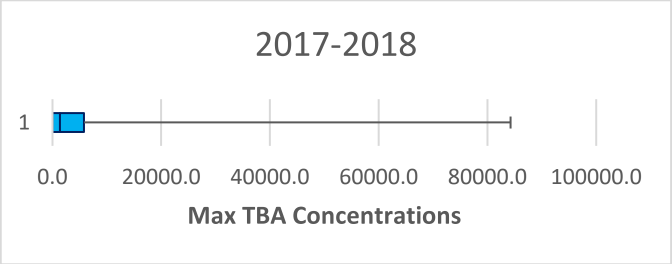


25 Percentile	290
Median	1343.7
75 Percentile	3861.3
Minimum	14
maximum	6750

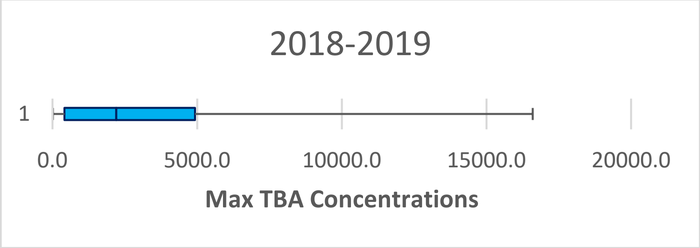
Statistical Data for SVE



25 Percentile	6.5
Median	28.5
75 Percentile	625.5
Minimum	0
maximum	4300



25 Percentile	13.7
Median	1350
75 Percentile	5800
Minimum	0
maximum	90300



25 Percentile	414
Median	2200
75 Percentile	5800
Minimum	0
maximum	90300

Figure 5-2. TBA concentrations remaining in closed LUST sites with DPE, AS, and SVE employed.

Other remedial methods, such as chemical oxidation, free product removal, and bioremediation were not implemented as often. No bioremediation was implemented for cases closed during 2016-2017 and 2018-2019. Bioremediation was employed only in one case during 2017-2018.

Table 5-2 shows the percentage of the closed cases in which TBA remained greater than the NL after remediation was completed.

Table 5-2. Percent of TBA Closed Cases with TBA Concentrations Higher than 12 μg/L after Remediation

Year	DPE	SVE	AS	Chemical Oxidation	LNAPL Removal	Bioremediation
2016-2017	63%	57%	63%	NI	50%	NI
2017-2018	68%	75%	63%	88%	100%	100%
2018-2019	94%	78%	89%	100%	100%	NI

NI: Not Implemented

MTBE versus TBA

To evaluate whether the employed remedial methods have equally been effective to treat MTBE and TBA, maximum concentrations of MTBE and TBA remaining at closure were obtained for each case for which numerical value was reported. The percent difference between TBA and MTBE concentration was then calculated as follows:

$$\%\ \text{Difference} = \frac{\text{Max TBA Concentration} - \text{Max MTBE Concentration}}{\text{Max MTBE Concentration}} \times 100\%$$

Equation 5-1

The average of the data were then obtained and tabulated. As seen in Table 5-3, an extremely large percent difference exists between TBA and MTBE concentrations. This points to the fact that the employed remedial methods were not nearly effective in reducing TBA concentrations as compared with MTBE concentrations.

Table 5-3 – Average Percent Difference between Maximum TBA and MTBE Concentrations Remaining in Closed Cases

Year	% Difference
2016-2017	36,127.1
2017-2018	539,796.0
2018-2019	184,598.4

Conclusion

- The median TBA concentrations remaining in the groundwater at the sites for which DPE was implemented for 2016 through 2019 were 83 µg/L, 1300 µg/L, and 3,800 µg/L, respectively. This averages out to be about 1728 µg/L.
- The median TBA concentrations remaining in the groundwater at the sites for which AS was implemented for 2016 through 2019 were 230 µg/L, 1250 µg/L, and 1,343.7 µg/L, respectively. This averages out to be about 941 µg/L.
- The median TBA concentrations remaining in the groundwater at the sites for which SVE was implemented for 2016 through 2019 were 28.5 µg/L, 1350 µg/L, and 2,200 µg/L, respectively. This averages out to be about 1193 µg/L.
- In all of the three main remedial methods (except DPE during 2018-2019), the first quartile values of the TBA concentrations were much closer to the median than the third quartile were to the median. This shows that the higher TBA concentration values were much more dispersed than the lower values. These high concentrations remaining after closure point to the inefficiency of the three remedial methods.

- The data show that a combination of the routine and conventional groundwater remedial methods were able to reduce TBA concentrations in groundwater by as much as 90%. However, TBA remained at concentrations above 12 µg/L, in as high as 94% of these cases after completion of the three main remedial methods (DPE, AS, and SVE). In addition, aerobic bioremediation which appears to be the most effective method of TBA treatment was only employed at one case during the time investigated.
- The remedial methods were not nearly as effective in reducing the TBA concentrations as compared with the MTBE concentrations. This indicates that reducing TBA to safe levels in the groundwater requires specific and targeted approach.

References

California State Water Resources Control Board (2018), Division of Drinking Water https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/NotificationLevels.html. Accessed 27 December 2019

EPA Guide (2017) How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites. A Guide for Corrective Action Plan Reviewers. Available at https://www.epa.gov/ust/how-evaluate-alternative-cleanup-technologies-underground-storage-tank-sites-guide-corrective

Li Ke, Hokanson D. R., Crittenden J.C., Trussell R.R., Minakata D. (2008) Evaluating UV/H_2O_2 processes for methyl tert-butyl ether and tertiary butyl alcohol removal: Effect of pretreatment options and light sources, Journal of Water Research 42:5045-5053

Delisle S. (2019) Fact Sheet: Chemical Oxidation with peroxide-ex situ. National Research Council, Government of Canada. Available at https://gost.tpsgc-pwgsc.gc.ca/tfs.aspx?ID=22&lang=eng

Appendix A

California State Water Resources Control Board

Low-Threat Closure Policy Guidelines

1. General Criteria

General criteria that must be satisfied by all candidate sites are listed as follows:

a. The unauthorized release is located within the service area of a public water system;
b. The unauthorized release consists only of petroleum;
c. The unauthorized ("primary") release from the UST system has been stopped;
d. Free product has been removed to the maximum extent practicable;
e. A conceptual site model that assesses the nature, extent, and mobility of the release has been developed;
f. Secondary source has been removed to the extent practicable;
g. Soil or groundwater has been tested for MTBE and results reported in accordance with Health and Safety Code section 25296.15; and
h. Nuisance as defined by Water Code section 13050 does not exist at the site.

2. Media Specific Criteria

The most common exposure scenarios have been combined into three media-specific criteria:

I. Groundwater

The Groundwater-Specific Criteria are divided into five main categories:

(1)
a. The contaminant plume that exceeds water quality objectives is less than 100 feet in length.
b. There is no free product.
c. The nearest existing water supply well or surface water body is greater than 250 feet from the defined plume boundary.

(2)

a. The contaminant plume that exceeds water quality objectives is less than 250 feet in length.
b. There is no free product.
c. The nearest existing water supply well or surface water body is greater than 1,000 feet from the defined plume boundary.
d. The dissolved concentration of benzene is less than 3,000 micrograms per liter (μg/l), and the dissolved concentration of MTBE is less than 1,000 μg/l.

(3)

a. The contaminant plume that exceeds water quality objectives is less than 250 feet in length.
b. Free product has been removed to the maximum extent practicable, may still be present below the site where the release originated, but does not extend off-site.
c. The plume has been stable or decreasing for a minimum of five years.
d. The nearest existing water supply well or surface water body is greater than 1,000 feet from the defined plume boundary.

e. The property owner is willing to accept a land use restriction if the regulatory agency requires a land use restriction as a condition of closure.

(4)

a. The contaminant plume that exceeds water quality objectives is less than 1,000 feet in length.
b. There is no free product.
c. The nearest existing water supply well or surface water body is greater than 1,000 feet from the defined plume boundary.
d. The dissolved concentration of benzene is less than 1,000 µg/l, and the dissolved concentration of MTBE is less than 1,000 µg/l.

(5)

a. The regulatory agency determines, based on an analysis of site specific conditions that under current and reasonably anticipated near-term future scenarios, the contaminant plume poses a low threat to human health and safety and to the environment and water quality objectives will be achieved within a reasonable time frame.

II. Petroleum Vapor Intrusion to Indoor Air

Petroleum release sites shall satisfy the media-specific criteria for petroleum vapor intrusion to indoor air and be considered low-threat for the vapor-intrusion-to-indoor-air pathway if:

a. Site-specific conditions at the release site satisfy all of the characteristics and criteria of scenarios 1 through 3 as applicable, or all of the characteristics and criteria of scenario 4 as applicable; or
b. A site-specific risk assessment for the vapor intrusion pathway is conducted and demonstrates that human health is protected to the satisfaction of the regulatory agency; or

c. As a result of controlling exposure through the use of mitigation measures or through the use of institutional or engineering controls, the regulatory agency determines that petroleum vapors migrating from soil or groundwater will have no significant risk of adversely affecting human health.

Exception: Exposures to petroleum vapors associated with historical fuel system releases are comparatively insignificant relative to exposures from small surface spills and fugitive vapor releases that typically occur at active fueling facilities. Therefore, satisfaction of the media-specific criteria for petroleum vapor intrusion to indoor air is not required at active commercial petroleum fueling facilities, except in cases where release characteristics can be reasonably believed to pose an unacceptable health risk.

Scenario 1: Un-weathered LNAPL in Groundwater

Figure A-1 shows the required characteristics of the bio-attenuation zone for scenario 1:

1. The bio-attenuation zone shall be a continuous zone that provides a separation of at least 30 feet vertically between the LNAPL in groundwater and the foundation of existing or potential buildings; and 2. Total TPH (TPH-g and TPH-d combined) are less than 100 mg/kg throughout the entire depth of the bio-attenuation zone.

Un-weathered LNAPL is generally understood to mean petroleum product that has not been subjected to significant volatilization or solubilization, and therefore has not lost a significant portion of its volatile or soluble constituents (e.g., comparable to recently dispensed fuel).

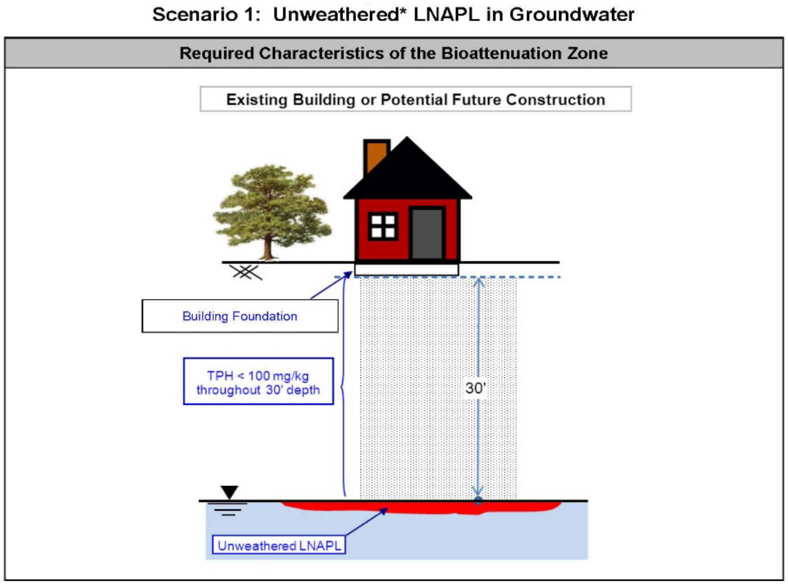


Figure A-1. Scenario 1: Un-weathered LNALP in Groundwater

Scenario 2: Un-weathered LNAPL in Soil

Figure A-2 shows the required characteristics of the bio-attenuation zone for scenario 2.

1. The bio-attenuation zone shall be a continuous zone that provides a separation of at least 30 feet both laterally and vertically between the LNAPL in soil and the foundation of existing or potential buildings, and 2. Total TPH (TPH-g and TPH-d combined) are less than 100 mg/kg throughout the entire lateral and vertical extent of the bio-attenuation zone.

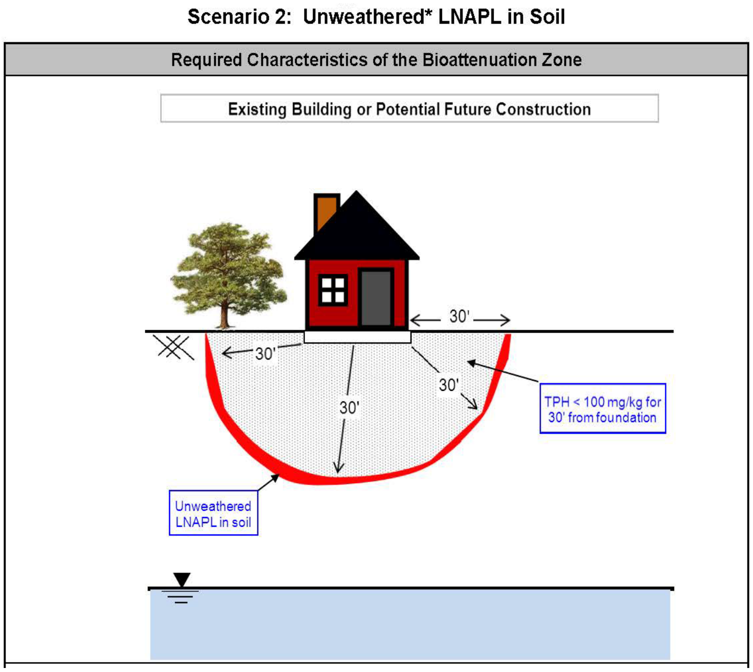
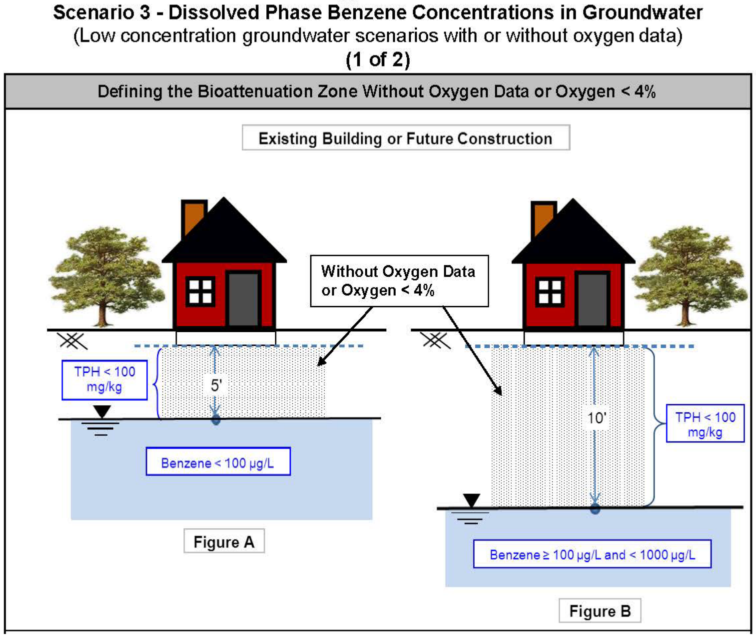
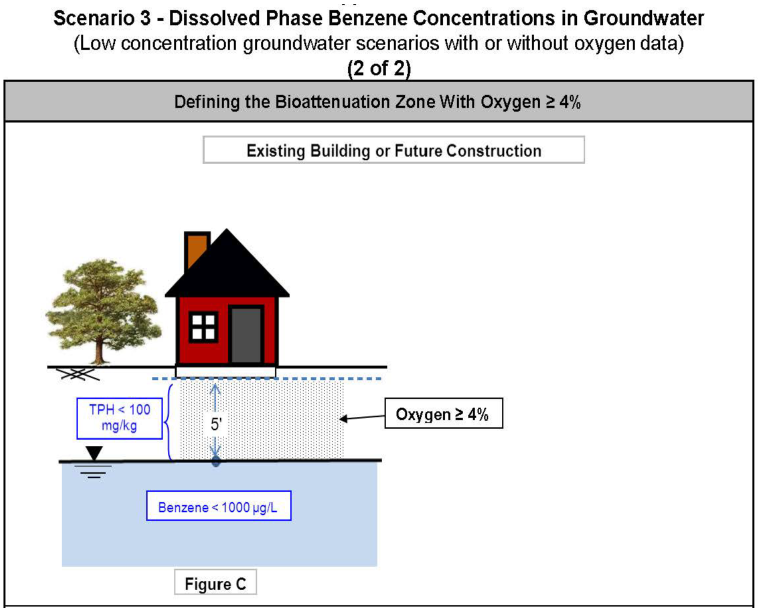


Figure A-2. Scenario 2: Un-weathered LNAPL in Soil

Scenario 3 - Dissolved Phase Benzene Concentrations in Groundwater (Low concentration groundwater scenarios with or without oxygen data)

Figure A-3 shows the required characteristics of the bio-attenuation zone for scenario 3.





Scenario 3 - Dissolved Phase Benzene Concentrations in Groundwater
(Low concentration groundwater scenarios with or without oxygen data)
(2 of 2)

Figure A-3. Scenario 3 Dissolved Phase Benzene Concentration in Groundwater

<u>Scenario 4 - Direct Measurement of Soil Gas Concentrations</u>

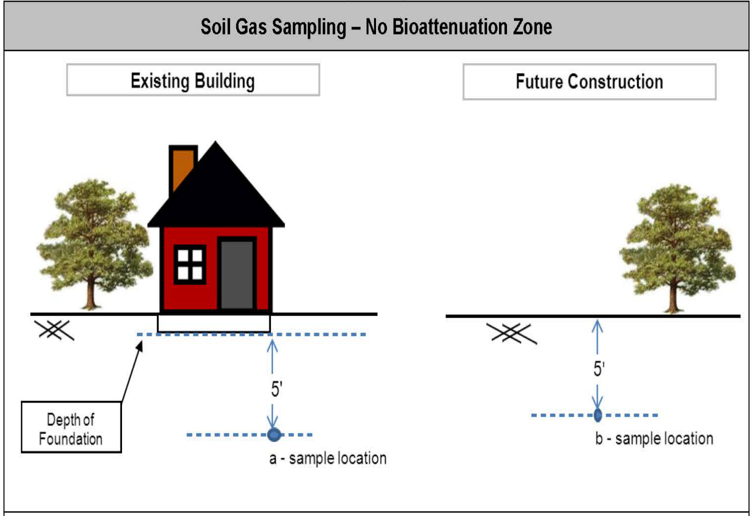
Figure A-4 shows the required characteristics of the bio-attenuation zone for scenario 4.

The criteria in the Table A-1 apply unless the requirements for a bio-attenuation zone, established below, are satisfied.

When applying the criteria below, the soil gas sample must be obtained from the following locations:

a. Beneath or adjacent to an existing building: The soil gas sample shall be collected at least five feet below the bottom of the building foundation.
b. Future construction: The soil gas sample shall be collected from at least five feet below ground surface.

Scenario 4 - Direct Measurement of Soil Gas Concentrations
(1 of 2)



Scenario 4 - Direct Measurement of Soil Gas Concentrations
(2 of 2)

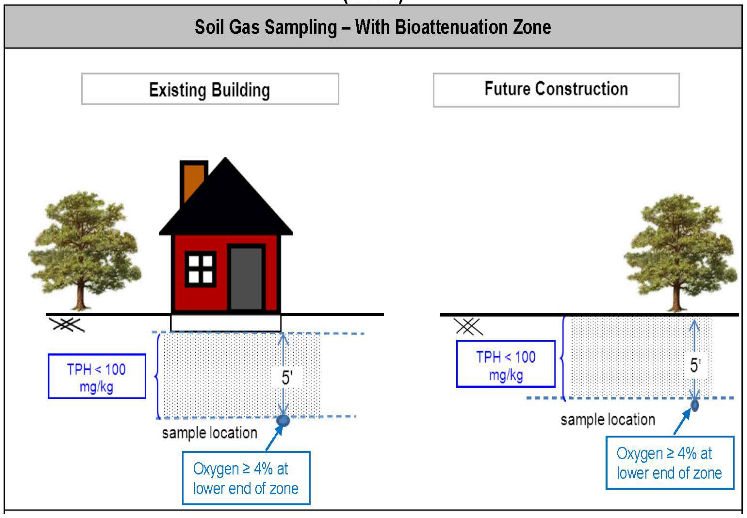
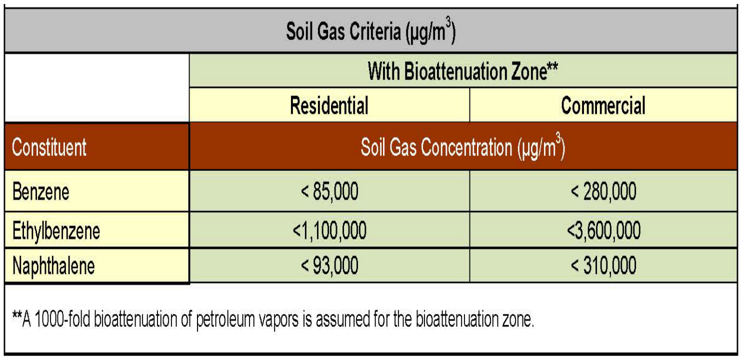


Figure A-4. Scenario 3 Dissolved Phase Benzene Concentration in Groundwater

Table A-1 – Soil Gas Criteria



Soil Gas Criteria ($\mu g/m^3$)		
	With Bioattenuation Zone**	
	Residential	Commercial
Constituent	Soil Gas Concentration ($\mu g/m^3$)	
Benzene	< 85,000	< 280,000
Ethylbenzene	<1,100,000	<3,600,000
Naphthalene	< 93,000	< 310,000

**A 1000-fold bioattenuation of petroleum vapors is assumed for the bioattenuation zone.

III. Direct Contact and Outdoor Air Exposure

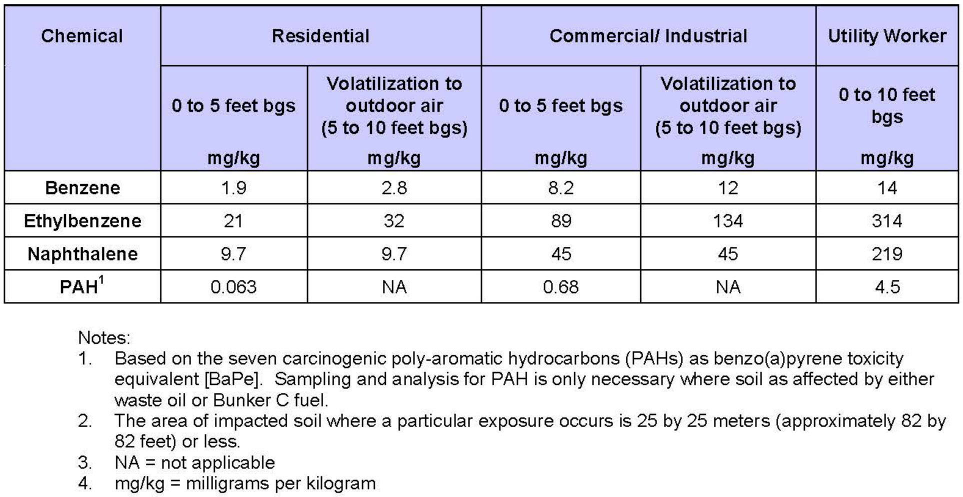
The LTCP describes conditions where direct contact with contaminated soil or inhalation of contaminants volatized to outdoor air poses a low threat to human health. Release sites where human exposure may occur satisfy the media-specific criteria for direct contact and outdoor air exposure and will be considered low-threat if they meet any of the following:

a. Maximum concentrations of petroleum constituents in soil are less than or equal to those listed in Table A-2 for the specified depth below ground surface (bgs). The concentration limits for 0 to 5 feet bgs protect from ingestion of soil, dermal contact with soil, and inhalation of volatile soil emissions and inhalation of particulate emissions. The 5 to 10 feet bgs concentration limits protect from inhalation of volatile soil emissions. Both the 0 to 5 feet bgs concentration limits and the 5 to 10 feet bgs concentration limits for the appropriate site classification (Residential or Commercial/Industrial) must be satisfied. In addition, if exposure to construction workers or utility trench workers are reasonably anticipated, the concentration limits for Utility Worker must also be satisfied.

b. Maximum concentrations of petroleum constituents in soil are less than levels that a site specific risk assessment demonstrates will have no significant risk of adversely affecting human health.

c. As a result of controlling exposure through the use of mitigation measures or through the use of institutional or engineering controls, the regulatory agency determines that the concentrations of petroleum constituents in soil will have no significant risk of adversely affecting human health.

Table A-2. Concentrations of Petroleum Constituents in Soil that will have no Significant Risk of Adversely Affecting Human Health



Chemical	Residential		Commercial/ Industrial		Utility Worker
	0 to 5 feet bgs mg/kg	Volatilization to outdoor air (5 to 10 feet bgs) mg/kg	0 to 5 feet bgs mg/kg	Volatilization to outdoor air (5 to 10 feet bgs) mg/kg	0 to 10 feet bgs mg/kg
Benzene	1.9	2.8	8.2	12	14
Ethylbenzene	21	32	89	134	314
Naphthalene	9.7	9.7	45	45	219
PAH[1]	0.063	NA	0.68	NA	4.5

Notes:

1. Based on the seven carcinogenic poly-aromatic hydrocarbons (PAHs) as benzo(a)pyrene toxicity equivalent [BaPe]. Sampling and analysis for PAH is only necessary where soil as affected by either waste oil or Bunker C fuel.
2. The area of impacted soil where a particular exposure occurs is 25 by 25 meters (approximately 82 by 82 feet) or less.
3. NA = not applicable
4. mg/kg = milligrams per kilogram

The policy emphasizes the importance of the site conceptual model and the vital role it has in identifying special attributes that might alter the regulatory agency's decision for closure.